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CHEMISTRY FOR SCHOOLS.

CHEMISTRY FOR SCHOOLS

AN INTRODUCTION

TO THE

PRACTICAL STUDY OF CHEMISTRY

BY

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WITH 100 ILLUSTRATIONS

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PREFACE.

THIS little work is intended as a sufficient Manual of Chemistry for Schools and junior Students, and as an aid to teachers wishing to introduce the science into the ordinary course of school study.

Its object is to supply a direct means of training the mind in habits of correct observation of facts, and of accurate reasoning from facts to generalisations; in other words, to cultivate scientific habits of thought. It is designed to set forth the methods which should be pursued in developing a knowledge of specific facts relating to the composition and changes of matter, and in endeavouring to group the facts so obtained into a consistent system by a chain of reasoning called a "Theory," thus constructing the elements of a Science of Chemistry.

To have attempted this in all its details, would have involved the reproduction of a considerable portion of the journals of chemistry for the last hundred years;

accordingly, many statements are made which must be taken for granted by the pupil, who must, however, understand that they rest on evidence of the same nature as those which are based on fully explained experimental proof.

The facts which are mentioned in the following pages were first made known to us through the observations of many illustrious men, and have been confirmed by their re-observation by countless other experimenters. The experiments described in illustration of them, with one or two exceptions, have been actually exhibited to classes of boys in the form given. Many have been performed by the boys themselves.

The author has made free use of the works of Graham, Miller, Nacquet, Odling, Watts, and Williamson, but is most of all indebted to the personal teaching of the last-named distinguished chemist. Reference to individual authorities is for the most part omitted in the text, as it is often impossible, and generally difficult, to trace a discovery home to its real parent. Mr. J. J. Bowery has kindly given the author much valuable assistance in preparing the book for the press.

Those who only wish to acquire a sufficient knowledge of chemistry to satisfy the moderate requirements of the London University Matriculation Examination, will not need to pay attention to anything beyond the chapters marked in the table of contents with a †.

HEAT, which is at present included under the head of chemistry in the Matriculation scheme, is not touched on, as it would require the addition of half as much matter again in order to treat it in anything like a satisfactory manner. Mr. Orme, the present teacher of experimental physics in University College School, has lately brought out a separate work on Heat, which will afford all the required information on the subject.

The list of apparatus needful for the performance of the experiments described, which is given at the end of the book, is drawn out on a more extensive scale than would be necessary for persons living in towns where breakages could be replaced at once.

DIRECTIONS TO THE READER.

In employing this book either for the purpose of private study, or of class teaching, it will be found advantageous, first, to go through the operations described under the title of "General Operations" on pp. 293—298, so as to familiarise all the pupils with simple manipulations and the technical names by which they are known. The next step will be to repeat as *many as possible* of the experiments described and alluded to in the successive chapters in the order in which they are set down. When it is impossible to repeat all the experiments, it will be necessary to pay close attention to the meaning of those which are omitted, as every one described has a direct bearing on the understanding of others.

In all cases, answers to the questions bearing on the matter studied at the time should be *written out* in full. Mere inspection of the question, and framing a mere verbal or mental answer, will lead to slovenly habits of thought.

When the student has thus worked through as far as the Chapter on Ammonia, he should read Chapter XXII.

Those pupils who have not a competent knowledge of arithmetic should not be allowed to attend to symbols and equations, but be confined to the study of the preparation and properties of the common non-metallic elements and their compounds; the

others will find no difficulty in making use of equations to express reactions, if they simply bear in mind, that the symbol of any element stands for that weight of it, which is called its atomic weight; thus, as a matter of fact, sixteen parts of oxygen unite with two parts by weight of hydrogen, to form eighteen parts by weight of water; but all this can be represented by writing down O + H + H = O H H, or $O + H_2 = O H_2$, it being understood that the writing side by side of two symbols does not imply multiplication, but only intimate chemical union of the elements represented by those symbols.

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CHEMISTRY FOR SCHOOLS.

CHAPTER I.

INTRODUCTION.

1. CHEMISTRY is a science which has for its ultimate object the determination of the constitution of the various forms of matter with which we are acquainted.

2. The attainment of this object is sought by the method of carefully examining the properties and composition of all known forms of matter, and classifying the results, so as to construct theories which shall embrace all the facts known at the time. As facts multiply, the theories which serve to connect them in a rational manner necessarily grow in generality, and will probably continue so to grow till they are comprehensive enough to include all the knowable facts concerning the nature of matter.

3. One of the first observations forced on the experimenter on different forms of matter is, that some things are obviously formed by the union or mixture of different bodies, while others are, to all appearance, simple, or composed of only one kind of matter.

ELEMENTS, or simple substances, are those which, in the present state of our knowledge, we are unable to divide into two or more *distinct* substances.

As examples of elementary bodies, we may take the metals, gold, silver, mercury, tin, lead, and zinc. By no known

process are we able to divide a portion of gold into anything but smaller pieces of the same metal. The other elements, such as oxygen, hydrogen, carbon, &c., &c., are also indivisible in this chemical sense.

4. COMPOUNDS are those bodies which we know to consist of more than one kind of matter, either because we can divide them into parts having distinct properties, or because we can produce them by causing two or more different substances to unite. As instances of compound bodies we may take brass, which is made by mixing copper and zinc, and which can be again split up into copper and zinc by suitable means; or water, which can be divided into the two elements, oxygen and hydrogen, or built up by causing the same two bodies to unite.

5. The elements at present known are about 63 or 64 in number. Of these comparatively few are important enough to engage the attention of beginners, either from their abundance, or from the extent of their chemical relationships. Each element, in addition to its full name, has a sign or symbol by which it is known. This symbol consists of the initial letter of the Latin name of the element, with another distinctive letter added when necessary. We shall subsequently see that the symbol of an element stands for something more than the name of it, and therefore cannot be used in all cases in lieu of the name itself. The following is a list of the most important elements with their symbols and their atomic weights.* (The names and symbols should at once be committed to memory).

SO-CALLED NON-METALLIC ELEMENTS.

NAME.	SYMBOL.	ATOMIC WEIGHT.
Oxygen . .	O	16
Hydrogen . .	H	1
Nitrogen . .	N	14
Carbon . . .	C	12
Sulphur . .	S	32

* The "atomic weights" of the elements are only introduced at this place to avoid having to repeat the table.

Name.	Symbol.	Atomic Weight.
Chlorine	Cl	35·5
Bromine	Br	80
Iodine	I	127
Phosphorus	P	31
Boron	B	11
Silicon	Si	28

Metallic Elements.

Name.	Symbol.	Atomic Weight.	Latin Name.
Potassium	K	39	Kalium.
Sodium	Na	23	Natrium.
Silver	Ag	108	Argentum.
Barium	Ba	137	
Calcium	Ca	40	
Magnesium	Mg	24	
Zinc	Zn	65	
Iron	Fe	56	Ferrum.
Manganese	Mn	55	
Aluminium	Al	27·5	
Copper	Cu	63·5	Cuprum.
Lead	Pb	207	Plumbum.
Mercury	Hg	200	Hydrargyrum.
Gold	Au	196	Aurum.
Bismuth	Bi	210	
Arsenic	As	75	
Antimony	Sb	122	Stibium.
Tin	Sn	118	Stannum.
Platinum	Pt	197	

CHAPTER II.

NATURE OF COMBUSTION—OXYGEN.

6. COMBUSTION is the commonest of all chemical phenomena. To ordinary observation it appears to be a wasting away of the body burnt, this wasting being accompanied by the production of heat and light in most cases. We will examine it experimentally, and try to discover what it really is.

1st. When a body is burnt, is anything lost, *i.e.*, is there a destruction of matter?

By means of a pair of apothecary's scales * weigh a porcelain crucible, record its weight, then coil up about a foot of magnesium wire, put it in the crucible, weigh again, and make a note of the weight of the two together; then heat the whole over a Bunsen's gas burner or a spirit lamp until the magnesium burns, avoiding as much as possible any loss of the white smoke formed. When combustion has ceased, allow the crucible and its contents to cool; then weigh again, when it will be found that there has been an *increase* in weight instead of a loss.

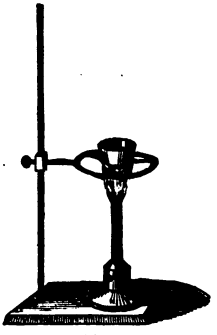


Fig. 1.

In this experiment some fragments of granulated zinc may be substituted for the magnesium wire; but then the heat will have to be stronger and to be continued for a longer time.

Observe, something has been gained—has been added to the original amount of matter in the crucible.

7. 2nd. From whence does this additional matter come? As nothing else but air was present during the experiment, it must come from that.

* See list of apparatus.

To see whether the air is consumed during the combustion of a body in it, float a porcelain crucible on the water of the pneumatic trough; put into it a bit of phosphorus* about the size of a large pea; light the phosphorus by touching it with a hot wire, and immediately cover the whole with a bell jar, or wide-mouthed bottle capable of holding about a pint and a half. The phosphorus will continue to burn for a little time and will then go out, although not all consumed. Allow the apparatus to cool, and then observe that the water has risen so as to fill about one-fifth of the bottle. One part out of five of the air contained by the bottle has been consumed or taken up by the burning phosphorus. Wait till the white fumes of phosphoric pentoxide, produced by the burning of the phosphorus, have subsided and dissolved in the water present, and then test the remaining gas with a lighted candle, which will be extinguished at once.

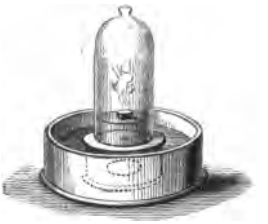


Fig. 2.

Observe, that the phosphorus burns at the expense of a portion, and only a portion, of the air.

It is possible to arrange an experiment so as to collect the phosphoric pentoxide produced, and to prove that it weighs exactly as much as the phosphorus burnt, plus the weight of that portion of the air used in burning it.

8. We have proved by the foregoing experiments that when a body burns, it takes something from the air, which something it adds to its own substance, thereby increasing its weight. The next step is to isolate that portion of the air which supports combustion. Lavoisier originally performed the following experiment: he kept mercury at a temperature near its boiling point for many days in contact with a known volume of air. At first, absorption took place; but after a time ceased—while at the same time red scales were formed on the surface of the metal. One-fifth of the air disappeared, and the remainder was no longer capable of supporting combustion. He heated the red

* Dry the phosphorus by pressure in blotting paper, or it will spurt on being lighted.

scales to a much higher temperature than that at which they were formed—and thereby resolved them into quicksilver (*i. e.* mercury), and a colourless gas which had the power of supporting combustion more brilliantly than air, and which, when added to the portion of air left in the first part of the experiment, restored all its original properties. He named the gas oxygen, and the compound which it formed with mercury oxide of mercury.

9. Heat a quarter of an ounce of well dried oxide of mercury in an apparatus constructed as shown in fig. 3, taking care to

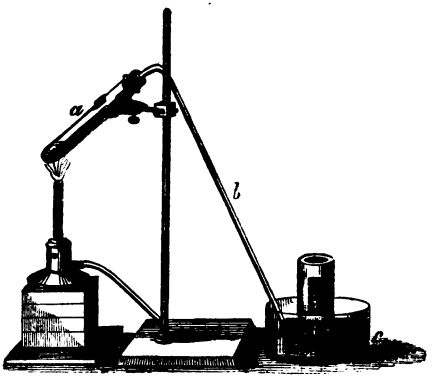


Fig. 3.

heat the glass slowly at first, and to keep the lamp moving enough to make it heat all the bottom of the test tube evenly, or the glass will crack. At the first application of heat, bubbles of air will come off from the end of the delivery tube; they may be allowed to escape. After a short time, tiny globules of mercury will collect on the upper part of the test tube, showing that decomposition has commenced. Now collect the escaping bubbles by holding a small bottle, or a test tube filled with water, over the mouth of the delivery tube. As each tube is filled, remove it from the water, after closing its mouth with your thumb, and put into the gas the glowing end of a splinter

of wood which has been lighted and blown out. As soon as all the air has been swept out of the apparatus, you will find that the wood is re-lit with a little pop, and continues to burn for a few seconds with a very brilliant flame.

10. If the quantity of mercuric oxide employed in this experiment were 216 grammes, and if the whole of it were decomposed and the products weighed, it would be found that 200 grammes of mercury and 16 grammes of oxygen resulted from the operation. And if any other quantity of the oxide were employed, the two products would bear the same proportion to one another. Now let the 200 parts of mercury be represented by the symbol Hg, and the 16 parts of oxygen by O, then the 216 parts of the oxide of mercury can be represented by writing the two symbols side by side thus, HgO. Further, we can represent the decomposition which takes place under the action of heat by separating them again, thus,—

$$HgO = Hg + O;$$

which equation not only shows that oxide of mercury decomposes into mercury and oxygen, but also shows that any quantity of it yields $\frac{16}{216}$ of its weight of the gas, and $\frac{200}{216}$ of its weight of mercury.

11. To prepare oxygen for the purpose of examining its properties, it is better to employ the body "chlorate of potash," or potassic chlorate, as it is more correctly called. Potassic chlorate contains the three elements—chlorine, potassium, and oxygen, and when submitted to the action of a strong heat it parts with all the last-named in a free state, leaving the first two combined with one another.

In a small porcelain basin place an ounce or two of potassic chlorate and heat it cautiously till it melts; let it cool, and powder the now thoroughly dry mass and preserve it in a bottle for use. Heat a quarter of an ounce of this dry salt in an apparatus like that before used for the decomposition of mercuric oxide, or if large quantities are wanted substitute a clean oil-flask for the test tube. It will first melt and then appear to boil, a phenomenon which is due to the escape of bubbles of

oxygen. After a time the evolution of gas will cease and the mass in the tube will become more infusible.

Collect the gas as it comes off in a number of wide-mouthed bottles at the pneumatic trough, and with it perform the experiments described in § 15.

12. If we take 122·5 grains (grammes, ounces, tons, &c.) of potassic chlorate, and decompose it, with suitable precautions to avoid loss, we obtain 74·5 grains (&c.) of the compound of chlorine and potassium (potassic chloride), and 48 grains (&c.) of oxygen. The 74·5 parts of potassic chloride consist of 35·5 parts of chlorine, and 39 parts of potassium, and 35·5 + 39 + 48 = 122·5 the weight of the salt taken. Let O stand as before for 16 parts of oxygen, and let the 39 parts of potassium be represented by K, and the 35·5 parts of chlorine by Cl; then potassic chlorate can be written $KClO_3$. We can, therefore, calculate the weight of oxygen gas contained in any weight of potassic chlorate, and how much we ought to get if we conduct its decomposition successfully. *E.g.*, let it be required to know how much oxygen is obtainable from 6·3 grammes of potassic chlorate. We first write out the equation of the decomposition,

$$KClO_3 = KCl + O_3 \text{ and quantify each term}$$

$$\underbrace{39+35{\cdot}5+48}_{122{\cdot}5} = \underbrace{39+35{\cdot}5}_{74{\cdot}5} + \underbrace{48}_{48}$$

∵ 122·5 parts potassic chlorate give 48 parts of oxygen

∴ 1 „ „ $\frac{48}{122{\cdot}5}$ and

6·3 „ „ $\frac{48}{122{\cdot}5} \times 6{\cdot}3 = 2{\cdot}47$ grammes,

nearly; or, by proportion,

$$122{\cdot}5 : 6{\cdot}3 :: 48 : 2{\cdot}47 \text{ grammes.}$$

Further, we can calculate how much potassic chlorate must be decomposed in order to obtain a desired weight of oxygen: *e.g.*,

Let it be required to be known how much of the salt we must use to get 135 grains of oxygen. Our equation tells us that to prepare 48 grains of oxygen, we must employ 122·5 grains of the salt; to get 135 grains of oxygen we must use as much more of the salt than 122·5, as 135 is greater than 48.

$$48 : 135 :: 122{\cdot}5 : 344{\cdot}5 \text{ grains.}$$

13. In order to completely decompose potassic chlorate into potassic chloride (K Cl) and oxygen, it is necessary to employ a strong and long-continued heat, which is often fatal to the generating vessel. By mixing with the potassic chlorate some fine dry powder which suffers no change itself at the temperature of the operation, the evolution of the gas is much facilitated. Powdered glass, sand, oxide of copper, oxide of manganese, &c., &c., serve the purpose almost equally well. The oxygen so obtained always contains a little chlorine; therefore, if pure oxygen is required the chlorate must be used alone. We do not yet know in what way these bodies aid the giving off of the oxygen, but give their action the name of catalysis, which means contact action.

14. When oxygen is wanted in large quantities for manufacturing purposes, or for the supply of the oxy-hydrogen blow-pipe, it is made by strongly heating in a fire the mineral "manganese," placed in an iron mercury bottle (fig. 4), fitted with an iron exit tube. "Manganese" is a binoxide of the metal manganese, consisting of 55 parts of manganese and 32 (16 × 2) parts of oxygen. Of this oxygen, $\frac{1}{3}$ is given off by the application of strong heat. As the black oxide of manganese is very cheap, this last plan is the most economical one for the preparation of oxygen on a large scale. The equation representing the change produced by heat is

Fig. 4

$$3\,(MnO_2) = O_2 + Mn_3O_4$$

$MnO_2 = 55 + 32 \therefore 3\,(MnO_2) = 261$, which quantity, as shown by the equation, gives 32 parts of oxygen and 229 parts of the body Mn_3O_4, which is called manganoso manganic oxide.

15. With the oxygen prepared by any of the processes described, perform the following experiments :—

1st. Fill a large test tube with the gas, into which plunge a splinter of wood which has been lighted and then blown out, so as to leave a glowing end. The wood will immediately burst into brilliant flame: this is very characteristic of oxygen, only one other gas doing the same. (See nitrous oxide.)

2nd. Introduce a lighted candle fixed on a wire into a bottle of the gas while a similar one burns outside. (Fig. 5.)

Fig. 5.

3rd. Light some sulphur in a deflagrating spoon (fig. 6), then put it into a bottle of oxygen; it will burn with an intense blue flame of great beauty.

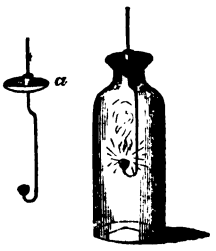


Fig. 6.

4th. Well dry a bit of phosphorus the size of a sweet-pea seed by carefully pressing it between folds of blotting-paper, and burn this in the gas in the same manner as the sulphur; it will burn with a light so white and brilliant as to be painful to the eyes.

5th. Resin, camphor, paraffin, &c., may be burnt with very brilliant effects.

6th. A piece of splintery wood-charcoal if ignited in a lamp, and then introduced into a large jar of oxygen at the end of a wire, will afford another good experiment.

7th. Twist together three or four strands of very fine iron wire; wind this rope round a thick glass rod to convert it into a spiral spring; fix one end to a cork, brighten the other end with a file, and then melt a little sulphur on to the bright part; inflame the sulphur and insert the helix into a tubulated jar of oxygen standing in a plate of water (fig. 7). The wire will be heated by the burning sulphur to a point at which it can begin to unite with the oxygen, which it will do with such energy that the wire will burn with great splendour, being at the same time converted into an oxide of iron, which will fall in molten drops through the water and burn into the plate.

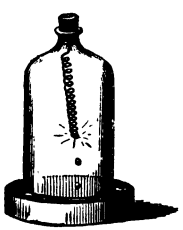


Fig. 7.

8th. Pass up into a tube, half filled with oxygen and standing in the

pneumatic trough, some of the gas called nitric oxide, when ruddy fumes will be formed, and will then be immediately absorbed by the water. This is quite characteristic of oxygen, as also is

the behaviour of a solution of pyrogallate of potash with oxygen. Half fill a tube with oxygen at the mercurial pneumatic trough, then pass up into the gas a solution of pyrogallic

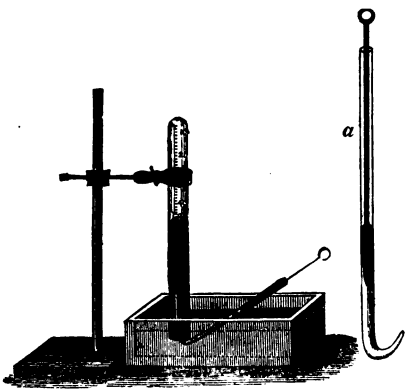


Fig 8.

acid in water, by means of a little squirt made from a bit of quill tubing, a wire, and some cotton wool; then some strong solution of potash by the same means. An immediate blackening of the solution will take place, the gas will be gradually absorbed, and the mercury rise to supply its place. If the oxygen is quite pure, the whole will be absorbed.

16. From the direct and indirect experiments quoted, we find that oxygen is colourless, tasteless, odourless, not very soluble in water (it was collected over water), that it readily and rapidly unites with a variety of bodies, producing the phenomenon of combustion, that it behaves with at least two reagents (see index), in a way which suffices to identify it, if it can be proved that no other bodies do the like. In addition to the properties illustrated by the above experiments there is another, or rather another form of one, viz., that of uniting slowly at

ordinary temperatures with other bodies. This power is best illustrated by the rusting of iron; or the conversion into oxides of the metals potassium and sodium, when exposed to air. Oxygen is the great supporter of animal life, a fact which might be negatively proved by confining a small animal, such as a mouse, in a portion of air from which the oxygen had been removed. It is not necessary to perform this experiment.

17. Besides being contained in the air, oxygen constitutes $\frac{8}{9}$ of water, and about $\frac{1}{2}$ of most common minerals; and it is also found in all animal and vegetable bodies. It is indeed the most abundant of all elements, forming about $\frac{1}{3}$ of the whole crust of the earth.

18. When oxygen is in the state of condensation due to a temperature of 0° Centigrade (32° Fahr.), and a pressure equal to the support of a column of mercury 30 inches, or 760 millimeters, in the barometer, 44·4 cubic inches of it weigh exactly 16 grains. At a temperature of 15° Centigrade (60° Fahr.) the same weight of oxygen occupies a space of 46·84 cubic inches; or on the metrical system of weights and measures, 16 grammes of oxygen at 0° Centigrade and 760 millimetres barometric pressure, occupy 11·2 litres, or 11,200 cubic centimetres.

These numbers are the results of experiments carried out with the greatest care and nicety by many distinguished chemists. A bare outline of their processes is all that can here be given, and is only introduced at all in order to give the student an example of the means adopted in determining the densities of gases.

A globe having a capacity of at least 200 to 400 cubic inches and fitted with a stopcock, is exhausted of air by the air-pump and weighed; oxygen (or other gas) dried by suitable means is then admitted into the globe, which is weighed again. The increase of weight will of course be the weight of the gas contained by the globe. The capacity of the globe must then be determined by filling it with water and again weighing, and from the weight of water it holds calculating how many cubic inches it measures. (A cubic inch of water weighs 252·456 grains; or on the metrical system, every gramme of water =

1 cubic centimetre). As the volume of a gas is subject to great alterations by change either of pressure or temperature, a number of precautions and corrections, which cannot fully be introduced here, have in practice to be adopted.

19. Knowing thus the volume of a certain weight of oxygen under stated conditions, it is easy to find that of any other weight under like conditions, *e.g.*, What is the volume at 0° Centigrade and 30 inches, barometric pressure, of 10 grains weight of oxygen. Since under these conditions—

$$\therefore \text{ 16 grains occupy } 44{\cdot}4 \text{ cubic inches}$$

$$\therefore \text{ 1 } \quad \text{,,} \quad \text{,,} \quad \frac{44{\cdot}4}{16} \text{ and}$$

$$\text{10 } \quad \text{,,} \quad \text{,,} \quad \frac{44{\cdot}4}{16} \times 10 = 27{\cdot}75 \text{ cubic inches.}$$

Or, if we substitute grammes for grains, and litres for cubic inches, in the same problem—

$$\therefore \text{ 16 grammes of oxygen occupy } 11{\cdot}2 \text{ litres.}$$

$$\therefore \text{ 1 } \quad \text{,,} \quad \text{,,} \quad \frac{11{\cdot}2}{16} \text{ and}$$

$$\text{10 } \quad \text{,,} \quad \text{,,} \quad \frac{11{\cdot}2}{16} \times 10 = 7 \text{ litres.}$$

Further, we can, of course, calculate with equal facility the weight of any given volume, *e.g.*, What is the weight of 15 litres of oxygen at the normal pressure and temperature?

$$11{\cdot}2 : 15 :: 16 : 21{\cdot}428 \text{ grammes.}$$

QUESTIONS ON CHAPTERS I. AND II.

1. What do you mean when you speak of a *simple* substance?
2. What do you mean when you speak of a *compound* substance?
3. On what evidence do we make the separation?
4. Give *examples* of elementary and of compound bodies?

5. About how many elements are at present known?

6. Is water an element?

7. How many so-called non-metallic elements are there?

8. When a body is burnt, is anything lost?

9. How could you prove the truth of your statement?

10. What part does the air take in the process of combustion?

11. Does the whole of the air help to support combustion?

12. By what process can we obtain oxygen from the air?

13. Describe the apparatus used for the preparation of oxygen?

14. What weight of oxygen and what of mercury could we obtain from 1 ounce (480 grains) of mercuric oxide?—*Ans.* 35·5 grains oxygen, and 444·5 grains mercury.

15. What do the symbols "Hg" and "O" respectively stand for.

16. Give the equation representing the decomposition of red oxide of mercury by heat.

17. Describe the preparation of oxygen from potassic chlorate.

18. (*a*) What is the *formula* of chlorate of potash? (*b*) What do the symbols K and Cl stand for, and what do you mean by O_3? (*c*) Represent its decomposition by heat by an equation. (*d*) By what means can you render its decomposition more easy?

19. Give equation representing the action of heat on manganic dioxide.

20. Quote some experiments to prove that oxygen is a very powerful supporter of combustion.

21. (*a*) What is the behaviour of oxygen with nitric oxide? (*b*) What with pyrogallate of potash? (*c*) Enumerate the chief properties of oxygen.

22. Name some of the principal natural bodies containing oxygen.

23. What is the weight of 100 cubic inches of oxygen (measured at 0° Centigrade or 32° Fahr., the barometer being 30 inches)? *—*Ans.* 36·04 grains.

24. What must be the capacity of a bottle which is to hold 9·3 grains of oxygen?—*Ans.* 25·807 cubic inches.

25. What volume will 100 grains of oxygen occupy?—*Ans.* 277·5 cubic inches.

26. How many cubic inches will 36 grains of oxygen occupy?—*Ans.* 99·9 cubic inches.

27. What volume will 100 grammes of oxygen occupy?—*Ans.* 70 litres or 70,000 cubic centimetres.

28. What is the weight of 100 cubic centimetres of oxygen?—*Ans.* 0·1428 grammes.

* In this and all subsequent questions involving the volumes of gases it is supposed that the gas is measured at a temperature of 0° centigrade (32° Fahr.), and at a pressure corresponding to 760 mm. (millimetres), or 30 inches barometric pressure, unless otherwise stated.

29. How many grammes of oxygen are contained by a bottle which is capable of holding 2·5 litres of water?—*Ans.* 3·571 grammes.

30. What weight of oxygen is contained in 70 grains of cupric oxide (CuO)?—*Ans.* 14·08 grains.

31. How much oxide of silver (Ag_2O) must I heat to get 50 grains of oxygen?—*Ans.* 725 grains.

32. What weight of $KClO_3$ must I use to get 200 grammes (grains) of oxygen?—*Ans.* 510·41 { grains. / grammes.

33. How many grains (grammes) of potassic chlorate must be decomposed to give 35 grains (grammes) of oxygen?—*Ans.* 89·3 { grains. / grammes.

34. If 480 grains (or grammes) of potassic chlorate are completely decomposed by heat, what weight of oxygen is given off?—*Ans.* 188 { grains, / grammes, } nearly.

35. What weight of oxygen will a kilogramme of manganic dioxide yield by the action of heat?—*Ans.* 122·6 grammes.

36. What weight and what volume of oxygen could I obtain from 55 grains of $KClO_3$?—*Ans.* 21·5 grains = 59·8 cubic inches.

CHAPTER III.

NITROGEN AND AIR.

20. *Nitrogen.*—In the course of examining into the nature of combustion, it was found that only about one-fifth of the air consisted of oxygen; the other four-fifths being some gas which had not the power of combining with the burning bodies under the conditions of the experiments. This larger portion of the air is the element nitrogen, which seems to act as a moderator of the energy of the oxygen.

Nitrogen can be obtained in a separate state by a variety of methods, either from the air or from other bodies containing it.

1°. From atmospheric air, by burning phosphorus in a portion of the latter confined in a bell-jar standing over water (see § 7). In this case the phosphorus unites with the oxygen of the air to form phosphoric pentoxide (P_2O_5), which dissolves in the water of the trough, leaving the nitrogen in a tolerably pure state.

Fig. 9.

21. 2°. By sending a slow stream of air from a gasholder first through a U tube, containing a plug of cotton wool to stop dust, then lumps of potash in one limb and calcic chloride in the other, then through a tube of hard glass containing copper turnings, kept at a bright red heat (by burning charcoal in the sheet iron furnace shown in fig. 10, or by gas in the furnace shown on p. 21). Nitrogen in a state of great purity may be obtained by collecting the escaping gas. In this case the copper (Cu) com-

bines with the oxygen to form cupric oxide (oxide of copper). In order to remove 16 grains of oxygen, it is necessary to use at least 63·5 grains of copper. Let Cu = 63·5, then oxide of copper will be represented by Cu O.

22.** 3°. Ammonia, which is one of the commonest compounds of nitrogen, serves very conveniently for its preparation. It consists of 14 (by weight) parts of nitrogen, represented by N, and 3 of hydrogen, represented by H_3, altogether NH_3. Pass a slow current of chlorine (see § 72) through a strong solution of this body in water contained in the bottle furnished with three tubes shown in figure 11. The chlorine unites with the hydrogen of the ammonia to form hydric chloride (H Cl), while the nitrogen escapes in the free state and can be collected over the pneumatic trough. The hydric chloride, as fast as it is formed, unites with undecomposed ammonia still present and forms hydrochlorate of ammonia (NH_3HCl). In this experiment the operator must be most careful to have a LARGE EXCESS of ammonia present during the whole time, or he will certainly have some chloride of nitrogen formed, which will almost as certainly explode violently. The reaction is represented by the equation

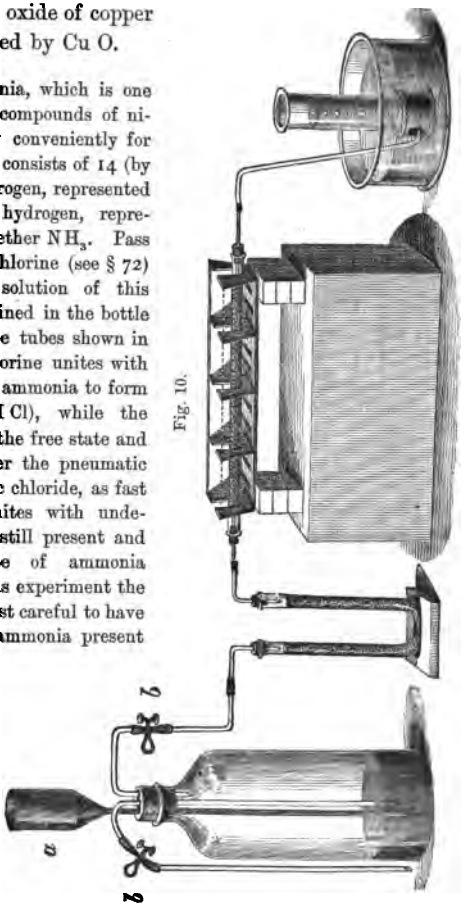


Fig. 10.

$$4(NH_3) + 3Cl = N + 3(NH_3HCl).$$

** Those paragraphs marked thus ** may be omitted by beginners.

23**. Nitrogen can also be made by heating ammonic nitrite ($NH_3 HNO_2$) which entirely breaks up into water and nitrogen—

$$NH_3 HNO_2 = N_2 + 2(H_2O).$$

Boiling its solution is quite sufficient to decompose the salt.

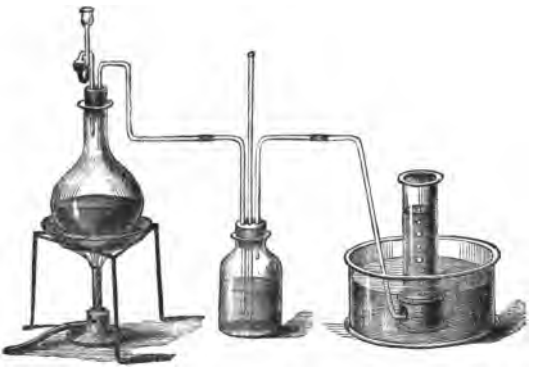


Fig. 11.

24. Nitrogen is, of course, colourless, tasteless, and inodorous. We have proved that it does not burn or support combustion; and that, if at all soluble in water, it is so to a very slight extent. By careful experiments it can be shown to be slightly soluble in water, though to even a less extent than oxygen is. By confining any small animal in a vessel of nitrogen we can prove that it does not support life, while the fact that we inhale it constantly proves that it is not poisonous. The properties of nitrogen are indeed nearly all negative.

25. Besides constituting $\frac{4}{5}$ of the atmosphere, nitrogen occurs in all animal bodies except fat, and in all parts of plants except starch, woody fibre, gum, sugar, and oil. The proofs of these statements will be given under the head of Ammonia.

26. 44·4 cubic inches of nitrogen, at the normal temperature and pressure, weigh 14 grains, or 11·2 litres of it weigh 14 grammes; hence, bulk for bulk, it is as much lighter than oxygen as 14 is less than 16.

27. *Air.*—We have proved that the air contains both oxygen and nitrogen, and have effected a rough quantitative determination of their amounts. In addition to these two gases, air always contains several other bodies in smaller proportions. Of these minor constituents, carbonic dioxide (CO_2) and water vapour are the two most important, ammonia and nitric acid being present also in exceedingly small quantity. Their presence can be demonstrated by the following experiments :—

1. Expose to the air some fragments of calcic chloride, (chloride of calcium), which will become liquid in the course of a few hours from the absorption of moisture.

2. Make a frigorific mixture of powdered ice and salt; put it into a flask and expose to the air. In a short time the flask will be covered with a hoar frost (congealed water deposited from the air).

3. Carbonic dioxide is detected by exposing some lime water or baryta water, either of which bodies will absorb the acid gas from the air, forming carbonates of lime or baryta: these carbonates being insoluble, will precipitate and so turn the liquid milky.

28. A moderately accurate volumetric analysis of air may be effected in the following way: Into a graduated tube (fig. 12), standing over water, introduce some air; note the volume it occupies when the water is the same height inside and outside the tube. Then push up into the air a bit of phosphorus on the end of an iron wire;* leave the phosphorus in contact with the air till no further absorption takes place: at the end of which time withdraw it, and again bring the water inside the tube to a level with that outside, by depressing the tube in the trough. It will then be found that a decrease in volume has taken place in the proportion of nearly 21 volumes for every 100 volumes originally included in the tube.

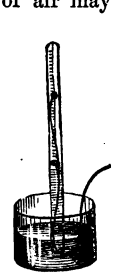


Fig. 12.

As the diminution of volume is due to the absorption of

* To fix the phosphorus to the wire, make a loop at the end of the latter; melt a little piece of phosphorus under water in a test tube, put the loop of the wire into it, and then allow the whole to cool, when the phosphorus can be withdrawn with the wire.

oxygen by the phosphorus (phosphoric trioxide P_2O_3 being formed), we find by this experiment that air consists of about 21 measures of oxygen and 79 measures of nitrogen in every 100 parts by *volume*.

29. Or a more accurate analysis could be made by measuring off some air in a graduated tube standing over mercury, and passing up into it a solution of pyrogallic acid in strong potash solution, by means of the little squirt figured in the margin (fig. 13). As before shown, oxygen is absorbed by this reagent, but nitrogen is not; therefore, if the volume of the gas remaining after action has ceased be measured again, the proportion of the two bodies will be obtained. Yet another and still more accurate way will appear when discussing the composition of water.

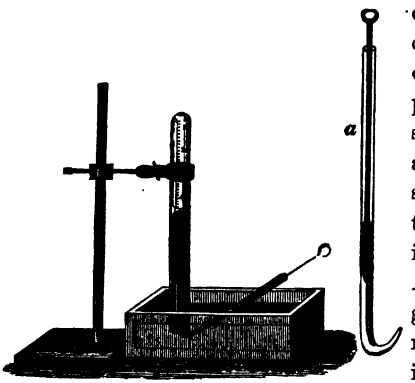


Fig. 13.

30. As gases have volumes inversely as the pressure on them, and as the column of mercury in the tube balances a portion of the atmospheric pressure, it is necessary, when measuring a gas, either to sink the tube in the metal till there is no difference in level between the inside and outside portions, or to make a correction of the observed volume, thus: Subtract the difference (in inches) between the level of the mercury in the tube and that in the trough from the height of mercury in the barometer at that moment. This difference will express, in inches of mercury, the pressure which the gas in the tube actually sustains.

As this must be less than the whole atmospheric pressure, the observed volume of the gas will be as much too *great* as the pressure it is subject to is less than that due to the whole pressure of the air (which is equal to sustaining on an average a column of mercury 30 inches or 760 mm. high), therefore the observed volume must be reduced in a like proportion.

To take an example. Suppose in our experiment the volume observed was 59 cubic centimetres, and that the mercury inside the tube was 3 inches higher than outside, while the barometer stood at 30 inches. The pressure at which the gas is measured is $30-3=27$, *i. e.* $\frac{27}{30}$ of the whole atmospheric pressure, therefore its observed volume must be $\frac{30}{27}$ of its true volume (x).

$$\because \frac{30}{27}x = 59$$

$$\therefore \quad x = 53{\cdot}1.$$

31. The determination of the composition of air by weight is an operation of too much difficulty to be attempted by the student. As, however, the composition of air is a very important point, an outline description of the method and apparatus employed by Dumas and Boussingault is appended, together with a figure.* A large glass globe, furnished with a stop-cock, was exhausted and weighed. A tube of hard glass, filled with finely divided metallic copper, and provided with stop-cocks, was also exhausted and weighed, and placed in a cold furnace, and connected with the globe; the other end was then provided with a series of U tubes, the first two (d, d) containing pumice stone soaked in oil of vitriol, and the second (e) lumps of solid potash. All parts of the apparatus being

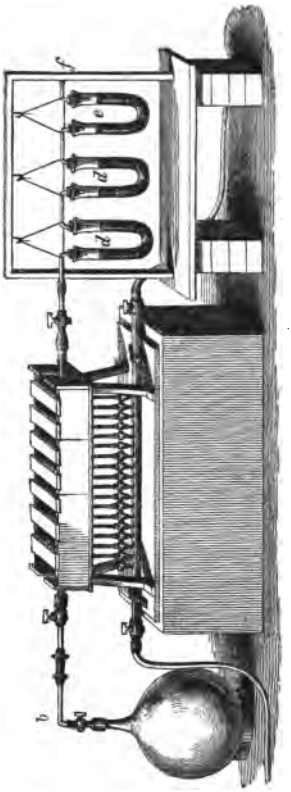


Fig. 14.

* The apparatus is slightly modified.

connected, and proved to be air-tight, the tube (*b*) was brought to a red heat, and then the stop-cocks of the exhausted globe and of the tube were slowly opened. Air, of course, entered at *f*, and left its carbonic dioxide, combined with the potash, in the tube marked (*e*); then, in passing onwards, its moisture combined with the oil of vitriol in (*d d*), and on entering the tube of copper, it was wholly deprived of its oxygen, which united with the copper to form oxide of copper, while the nitrogen alone passed on into the globe. Now, as the weight of the globe, when empty, was known, it was only necessary to weigh it again at the end of the experiment to ascertain how much nitrogen had entered it; and as the tube of copper was heavier than before, by as much as the weight of the oxygen which had combined with the metal, it was only necessary to add these two increases together, in order to find how much pure air had entered the apparatus; while the individual increases of course gave the proportions in which oxygen and nitrogen existed in that quantity. For example, let us suppose that the globe increased 3·85 grammes in weight, and the tube 1·15 grammes; then the weight of air which had entered the apparatus was 5·0 grammes (3·85+1·15), and as 5·0 : 3·85 : : 100 : 77, the percentage of nitrogen in air by weight, and 5·0 : 1·15 : : 100 : 23 the percentage by weight of oxygen in air, which are, indeed, the true numbers. Knowing the percentages by weight of oxygen and nitrogen in pure air, and knowing the specific gravities of the two gases, it is easy to calculate their proportions by volume. Do it as an exercise.

The proportions of the two gases in pure air are, therefore, found to be—

	Volume.	Weight.
Oxygen . . .	20·8	23
Nitrogen . . .	79·2	77
	100·0	100

32. The amount of water and of carbonic dioxide gas present in the air of any locality at a given time, may be determined with great nicety by

causing a known large volume of it to pass first through a couple of weighed U tubes containing pumice stone soaked in oil of vitriol, and then through another, also weighed, containing soda lime (a mixture of lime and caustic soda). The increase in the weight of the first tubes gives the weight of water as vapour in the air used, and that of the last the weight of carbonic dioxide. The volume of air used being known, it is easy to calculate its weight (see § 34), and from all these data to find the percentage proportions.

The amount of water vapour present in air varies within very wide limits, 0·9 per cent. by weight being near its average quantity. The carbonic dioxide is in still smaller proportion, being indeed only about 4 to 6 parts in 10,000 of air.

33. Having determined the composition of air, it remains to examine its constitution, *i.e.*, to find out whether the oxygen and nitrogen are in a state of chemical union, or only intermixed. Now, a *chemical compound* possesses properties of its own as distinguished from the properties of its constituents; but we find that air has no chemical characteristics which are not possessed by a simple mixture of the gases composing it. Indeed, we find that, on mixing oxygen and nitrogen together in the proper proportions, we get no rise of temperature, which proves that no union has taken place; yet the mixture has all the physical and chemical properties of pure atmospheric air. A *compound* dissolves in water without change of proportional composition; but the air which is dissolved by water contains a larger proportion of oxygen than 20·8 per cent. of its volume. This last fact arises from oxygen being more soluble in water than nitrogen is, and from the two gases dissolving in water each in proportion to its individual solubility, and the amount of pressure which it exerts on the liquid. Air, therefore, does not act as a *whole*, but as a thing of parts, having properties distinct from one another, which properties are exerted independently, as if each part existed by itself; we, therefore, consider air to be a mere *mixture* of its constituents.

The proof of the last statement is easy. Fill a Florence flask quite full of common water which has been exposed to the air for some time; fit to it a cork and delivery tube, as shown in fig. 15, and let this last terminate

inside a graduated tube containing a solution of caustic soda, and standing in a small basin of the same liquid. Apply heat to the flask till the water boils, and continue to boil it for ten minutes. Gases are much less soluble in hot than in cold water, therefore the oxygen, nitrogen, and carbonic dioxide, which were dissolved in the water, will be expelled and will be driven together with steam into the solution of soda. The steam will condense, and the carbonic dioxide will combine with the alkali, while the

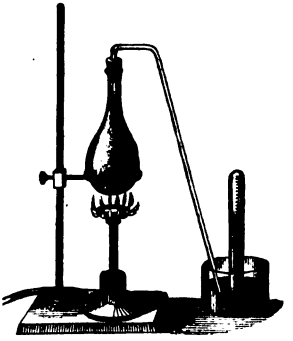


Fig. 15.

Fig. 16.

mixed oxygen and nitrogen will rise to the top of the graduated tube. Transfer the tube and its contents to a large pan of cold water so that the gas may become cool, and the heavy soda solution sink out of the tube and be replaced by water. Introduce a piece of phosphorus on the end of a wire as in the analysis of air, when it will be found that *one-third* of the gas is absorbed, whereas only *one-fifth* of the air which has not undergone solution consists of oxygen.

Other proofs of the want of chemical union between the components of air will be given after studying some of the true *compounds* of oxygen and nitrogen.

34. At the normal temperature and pressure, 44·4 cubic inches of air weigh 14·4 grains, or 11·2 litres weigh 14·4 grammes. Oxygen is, therefore, heavier than air as 16 : 14·4, and nitrogen lighter as 14 : 14·4.

QUESTIONS ON CHAPTER III.

1. Describe the preparation of nitrogen from air by the copper method.

2. How would you prepare nitrogen from ammonia? What precaution must you take?

3. In what bodies does nitrogen occur?

4. If a given bulk of oxygen weighs 10 grammes, how much will the same volume of nitrogen weigh?—*Ans.* 8·75 grammes.

5. How would you demonstrate the presence of (*a*) water vapour, and (*b*) carbonic dioxide in air.

6. Describe an experiment which shall show the proportion of oxygen to nitrogen in air by volume. What is that proportion in 100 parts?

7. How is the proportion of oxygen to nitrogen by weight determined, and what is it?

8. In a room 20 × 23 × 12 feet, how many cubic feet of oxygen are there?—*Ans.* 1148·16 cubic feet.

9. How many cubic feet of oxygen are contained in a room 12 feet long, 10 feet wide and 9 feet high?—*Ans.* 224·64 cubic feet.

10. How many grammes of each constituent are there in 100 grammes of air?

11. Is air a compound or a mixture? What experiments throw light on its constitution?

12. What is the weight of 100 cubic inches of nitrogen?—*Ans.* 31·5 grains.

13. How many kilogrammes of air are required to furnish 35 kilogrammes of oxygen?—*Ans.* 152·17 kilogrammes.

14. How many litres of air are required to furnish 25 kilogrammes of oxygen?—*Ans.* 84134·6 litres.

CHAPTER IV.

WATER AND HYDROGEN.

35. WATER, which next to air is the commonest and most ever-present of bodies, will form the next subject of examination.

We will first solve the problem, "Is it an elementary or a compound body?" To do this, it is necessary to act on it by other bodies, which must be admitted to be what they are described to be.

Confine about half an ounce of iron filings between two plugs of asbestos in a bit of hard glass tube of half-inch bore and about a foot in length. Connect one end of this tube with a flask for boiling water, and the other with a delivery tube leading to the pneumatic trough. Arrange the tube with the filings so as to slant slightly towards the flask, for which purpose

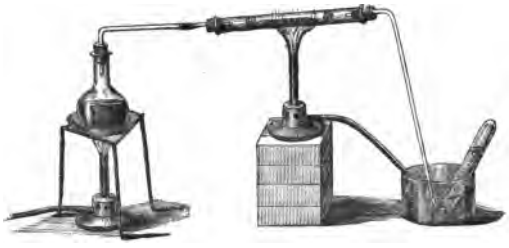


Fig. 17.

nothing is more convenient than the clip shown on fig. 18; heat the metal to redness by means of a lamp or red-hot charcoal, and then make the water in the flask boil briskly. The steam, *i.e.*, water vapour, will pass over the heated iron which will by it be converted into oxide of iron. In the receiver placed over the end of the delivery tube a gas will collect. This gas will be found to be neither oxygen nor nitrogen, for on applying a light to it it will burn with a pale blue flame; it is called hydrogen.

Admitting that iron is an element, this experiment amounts to proof that water is not one; for the metal takes from it oxygen, and sets free at the same time something else. Set aside the oxide of iron produced in the operation for further experiment.

36. Having, by this *analytical* method, shown that water is a compound body consisting of the combustible gas, hydrogen, and some other, which we have assumed to be oxygen, we will complete the proof of its qualitative composition by a synthetical experiment.

Pass hydrogen obtained by any of the methods described in §§ 37, et seq., through a U tube filled with fragments of calcic-chloride, or pumice soaked in oil of vitriol, to dry it; allow the gas to issue from the apparatus until all air is swept out (otherwise a violent explosion will take place) and

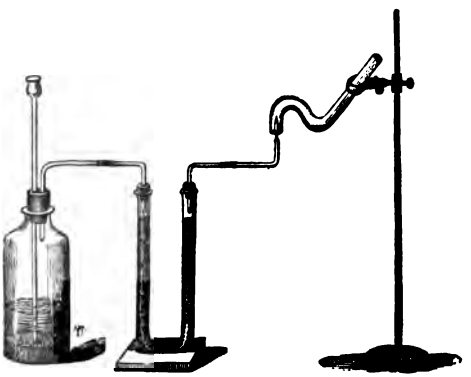


Fig. 18.

then light it at the jet which is situated directly under the mouth of the curved tube. The products of the combustion (*i.e.*, combination with oxygen) of the hydrogen will pass into the long arm of the said tube, and will there be condensed by the cold walls in the form of drops of water, which will run down and collect in the bend.

Here we have nothing present but hydrogen, oxygen, and nitrogen; dismissing the last from consideration, as not taking part in combustion, we observe that the water not only is a

compound, but consists of only two bodies, viz., oxygen and hydrogen.

37. Hydrogen, which is thus found to form an essential part of water, is contained in numberless other bodies, such as the hydrated acids, alkalies, organic substances of all kinds, &c., and can be produced from many of them by processes similar in principle to the one by which we obtained it from water, viz., by replacing it by some other element. The most convenient ways of obtaining pure hydrogen are the following :—

An apparatus of the kind described below is to be fitted up. In doing so it is well worth while to take some pains, as it is one much used for other purposes.

A wide-mouthed bottle, having a capacity of about one pint, is fitted air-tight with a cork, through which pass two tubes; one a short right-

Fig. 19.—Washing bottle with delivery tube.

Fig. 20.

angled piece open at both ends, the other a straight tube terminated by a funnel, and a foot or eighteen inches in length. By means of a bit of vulcanised caoutchouc tube, the apparatus may be attached to a washing bottle, fig. 19, the construction of which is explained by the diagram, or to a plain delivery tube leading to the pneumatic trough, as shown in fig. 20. Put into the bottle about four ounces of metallic zinc which has been granulated by being melted and poured into water; replace the cork and fill the bottle about one-third with water; then add a small quantity of hydric sulphate (oil of vitriol), H_2SO_4, by means of the funnel tube. In a short time a brisk effervescence, due to the escape of bubbles of hydrogen, will take place. The gas which first comes off is of course

mixed with the air which filled the upper part of the bottle; in time, however, it will sweep out all the air, and then may be collected in the usual manner. To be able to form any idea of the time required for this purpose, it is as well to collect the escaping gas and air in a jar at the pneumatic trough; when it amounts to about three or four times as much gas as would fill the generating vessel, you may consider your hydrogen sufficiently pure for most purposes. Or fill a test tube from time to time with the gas, and put a light to it. As long as there is air mixed with the gas a sort of whistling pop will be made; but when all is expelled, the gas will light with a plain pop and continue to burn at the mouth of the tube.

38. In the operation just described, the element zinc shoves out (if the expression may be allowed) the hydrogen of the hydric sulphate and takes its place; so that whereas we started with free zinc and hydric sulphate, we end with *free* hydrogen and zinc sulphate. The latter body may be obtained in crystals by evaporating the solution left in the bottle. The water is added to moderate the action and to prevent the liberated hydrogen exerting a secondary action on the excess of hydric sulphate present.

Let the formula H_2SO_4, in which $H = 1$; $S = 32$; and $O = 16$, stand for hydric sulphate, and let $Zn = 65$ of zinc, then we can represent the action which goes on in the bottle by the equation

$$H_2SO_4 + Zn = H_2 + ZnSO_4.$$

Now $H_2 = 2$; $S = 32$ and $O_4 = 16 \times 4 = 64$. $\therefore H_2SO_4 = 98$ and $Zn = 65$ $\therefore$ our equation states that if 98 parts of hydric sulphate be acted on by 65 parts of zinc, we shall get H_2, *i.e.*, two parts by weight of hydrogen, and $65 + 32 + 64 = 161$ parts of zinc sulphate. If to 98 parts of hydric sulphate we add, say 66 parts of zinc, 65 of those parts would dissolve, and the one part over would remain unacted on. Or, if 65 parts of zinc be added to an unlimited amount of hydric sulphate (diluted), they will only react on 98 parts, leaving the remainder unaltered. As 65 parts (grains, grammes, ounces, &c.) of zinc will thus liberate 2 parts of hydrogen, 1 part of zinc will set free $\frac{1}{65}$ as

much, that is, $\frac{2}{65}$ of its weight; 1 oz. of zinc will serve to displace $\frac{2}{65}$ of an ounce of hydrogen from any quantity of hydric sulphate that is sufficient to dissolve it. Or, as 98 parts of hydric sulphate yield 2 parts of hydrogen, 1 part will give $\frac{2}{98}$ of hydrogen .·. 1 ounce of oil of vitriol should give $\frac{1}{49}$ of an ounce of hydrogen, when treated with an excess of zinc.

39. Iron, in the form of filings, or small iron nails, may be employed instead of zinc to displace the hydrogen of hydric sulphate; but the hydrogen so obtained is very impure, and has a most unpleasant smell, due to the presence in it of compounds of hydrogen with sulphur, carbon, &c., derived from the impure iron. Instead of oil of vitriol we may employ hydric chloride (hydrochloric acid, muriatic acid) as the body from which to set hydrogen free by either of the above metals. The equations representing these reactions are—

$$a.\quad Fe + H_2SO_4 = H_2 + FeSO_4$$
$$b.\quad Fe + 2HCl = H_2 + FeCl_2$$
$$c.\quad Zn + 2HCl = H_2 + ZnCl_2.$$

Let Fe stand for 56 parts of iron, then it is shown that that quantity will displace as much hydrogen as 65 parts of zinc, and may be said, in this replacing power, to be equivalent to 65 parts of zinc; so, in replacing power, Fe = Zn.

Again, in equations *b* and *c* we see that 56 parts of iron, or 65 parts of zinc, replace 2 parts of hydrogen, and in doing so, combine with as much chlorine as those 2 parts of hydrogen were united to; therefore 56 parts of iron represented by Fe, or 65 parts of zinc represented by Zn, may be said to be equivalent (in combining power) to 2 parts of hydrogen represented by H_2.

40. Hydrogen can also be prepared by repeating the experiment described in § 35 on a larger scale. A three-foot length of iron gas tubing, the size of an ordinary gun-barrel, if filled with turnings of iron, heated in a charcoal furnace, and supplied with steam from a large flask, affords a very economical means of obtaining hydrogen for filling balloons, &c. The reaction is

$$4H_2O + 3Fe = H_8 + Fe_3O_4.$$

Fe_3O_4 is called ferrosoferric oxide, black oxide of iron, or magnetic oxide of iron.

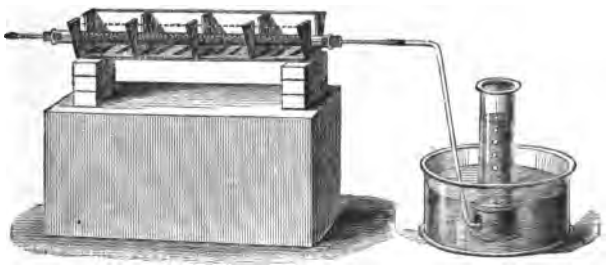


Fig. 21.

41. The metal sodium, when thrown into water, decomposes it, turning out *half* the hydrogen of that portion on which it acts. Let water $= H_2O$ and sodium $= Na = 23$, then the reaction is

$$H_2O + Na = H + Na\,H\,O \text{ (sodic hydrate).}$$

Hence we see that 23 parts of sodium are *equivalent* (in the same sense as before) to *one* of hydrogen.

To obtain hydrogen by this reaction, the best manner to proceed is to wrap up a piece of the metal of the size of a large pea in a fold or two of wire gauze, and then by means of a pair of crucible tongs to hold the little parcel firmly under the mouth of a small cylinder filled with water, and standing in the pneumatic trough. The water will be decomposed by the sodium, and the hydrogen find its way out through the meshes of the gauze. It is a dangerous experiment.

42**. Caustic alkalies, such as potassic hydrate (K H O) and sodic hydrate (Na H O), when heated dissolve metallic zinc, their hydrogen being replaced by that metal. The reaction is

$$2\,(K\,HO) + Zn = H_2 + Zn\,K_2\,O_2.$$

Here, as in the case of the other reactions in which zinc displaces hydrogen, we see that 65 parts of it displace 2 parts of hydrogen. This method of obtaining hydrogen yields it remarkably pure, but somewhat slowly. By adding a quantity of iron filings to the zinc, the action is much accelerated, although the iron itself undergoes no change, and seems to act only by its contact in the same way as a plate of copper

increases the rapidity with which a sheet of zinc dissolves in hydrochloric or sulphuric acid when immersed in contact with it.

43. The hydrogen obtained by either of these processes will of course be saturated with moisture, *i.e.*, will contain as much vapour of water as can exist in the space occupied by the gas at the temperature and pressure existing at the time of the experiment. Besides moisture, several impurities accompany the gas when prepared from commercial acids, and zinc, or iron. The principal ones are sulphuretted hydrogen, arsenuretted hydrogen, and when iron is employed, the vapour of an oily hydrocarbon. These require to be removed for many experi-

Fig. 22.

ments, an object which is accomplished by passing the gas through a series of U-shaped tubes, one containing fragments of caustic potash to retain sulphuretted hydrogen and some of the carburetted compounds; a second containing pumice-stone moistened with a strong solution of silver nitrate to stop the arsenuretted hydrogen; and a third, filled with pumice soaked in oil of vitriol, to absorb the last traces of the carbon compounds, and the whole of the moisture.

44. Hydrogen purified in the manner just described is perfectly colourless, tasteless, and inodorous, as may be safely proved by collecting some at the pneumatic trough, and inhaling a small quantity.

The following experiments may be tried with the gas which has undergone no purification, unless the contrary is stated:

1°. Fill a large test-tube or small cylinder with hydrogen at the pneumatic trough, lift it from the water, keeping its mouth downwards, pass a lighted taper fixed to a wire up into the gas. Observe that the flame of the taper is extinguished, but the hydrogen itself catches fire, and burns at the mouth of the jar, where the air and gas meet, with a pale blue almost invisible flame.

Fig. 23.

2°. Repeat the experiment after leaving a fresh filled jar open, mouth downwards, for one minute. Observe that the gas has been retained in the jar.

3°. Again repeat the experiment, after having kept the jar mouth upwards for the same time as in the last experiment. Observe that all the hydrogen has escaped.

4°. Collect some gas by upward displacement (as shown in fig. 23); here the gas, being lighter than the air contained in the jar, collects above it, displacing the heavier air in the same way as it does the still heavier water when the pneumatic trough is used. This method of collecting gases which are lighter than air is much used, and should be well practised.

5°. A small balloon, when filled with hydrogen, rises in the air because the material of the balloon, together with the hydrogen contained, weighs less than the air displaced. Soap-bubbles blown with hydrogen instead of air rise with great speed.

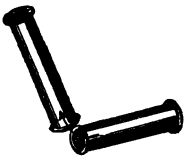


Fig. 24.

6°. Fill a jar with hydrogen, and pour the gas *upwards* through the air into another rather smaller jar held above the first, as shown in fig. 24. By means of a lighted taper prove that the hydrogen has left one tube and entered the other.

These experiments show hydrogen to be very light. It is indeed the lightest body known, 11·2 litres of it weigh only 1 gramme, therefore it is $\frac{1}{16}$ as heavy as oxygen, $\frac{1}{14}$ as nitrogen, and $\frac{1}{14.4}$ as air.

45. Mix a small quantity of plaster of Paris into a thick mud with water, spread it on a bit of filter paper, and press one end of a two-feet length of three-quarter inch tube on to it, and

hold it there till the plaster is set firmly. Allow the plaster to become *quite dry*, when you will have a tube closed at one end by a porous plug. Fill the tube by displacement with dry hydrogen, and immediately plunge its open end into water coloured with ink, litmus, &c., &c. At first the tube will be full of nothing but gas; but in a very short time the liquid will begin to rise in the tube, and will continue to do so till it is considerably higher inside than outside (fig. 25), showing that the hydrogen has escaped in part. Transfer the remaining gas to a graduated tube,* and pass up a bit of phosphorus on the end of a wire. Absorption will take place, showing that oxygen entered the tube (as air) at the same time that the hydrogen was leaving it. Fill the tube with air after drying the plug, fix it by india-rubber tubing to a U tube containing water, put

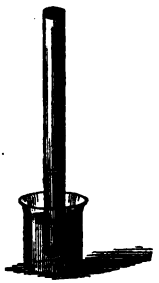


Fig. 25.

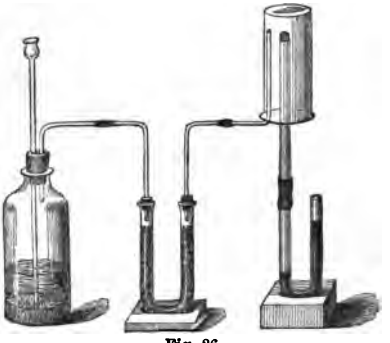


Fig. 26.

the porous end up into the big beaker kept full of hydrogen. (Fig. 26.) Now the liquid will be driven out of the tube, showing that hydrogen enters through the porous plug more

* By making it bubble up into it when filled with water at the pneumatic trough.

quickly than the air gets out. This spontaneous mingling of the gases is caused by their particles being always in rapid motion, so that they shoot into any space which is in communication with that which they occupy. The passing of one gas into the space occupied by another is called *diffusion.* The rate of diffusion will be obviously proportional to the rate of motion of the gas particles. If, in the experiments described, oxygen had been substituted for air, and the volumes of hydrogen and oxygen respectively which passed through the porous diaphragm had been measured, it would have been found that four measures of hydrogen passed for one of oxygen. Now oxygen is sixteen times as heavy as hydrogen, whence we see that these two gases have rates of diffusion inversely as the square roots of their densities.

All gases diffuse into one another as oxygen and hydrogen do, and the rates of their diffusion follow the rule given. The existence of this diffusion of gases explains why oxygen, which is as much heavier than nitrogen, as 16 is greater than 14, does not settle out of the air and form a layer on the surface of the earth.

46. When hydrogen is burnt from a metal jet, *e.g.*, that of a blowpipe, it gives a pale blue flame, hardly visible in dust-free air by daylight. Though incapable of giving much light, the flame is very hot, as can be shown by holding a small coil of very fine platinum wire in it, which will be raised to intense whiteness. The soda in a glass jet makes the flame yellow.

We have proved that ordinary combustion consists of rapid union of the combustible with the oxygen of the air. Combination can only take place when and where the particles of the combustible come in contact with the oxygen, therefore, combustion takes place only on the surface which connects the burning body with the air. But if we make a mixture of a combustible gas with a quantity of air or oxygen sufficient to consume it, and then heat the mixture to such a temperature that the two can unite, the mass will burn all through at once. As great heat is produced, the product is expanded violently,

and displaces, or tends to displace, surrounding matter, causing, indeed, what is called an explosion.

Make a mixture of two volumes of hydrogen with one of oxygen or five of air, in a soda water bottle, wrap the bottle in a stout cloth and apply a light to its mouth, it will "go off" with a noise like a gun, because the air round the mouth of the bottle is made to vibrate rapidly and irregularly. The vibrations reaching the ears produce the sensation of sound.

47. Pass dry hydrogen over ignited oxide of lead * confined between two plugs of asbestos (a fibrous mineral which is little affected by heat) in a tube made by softening a foot and a half

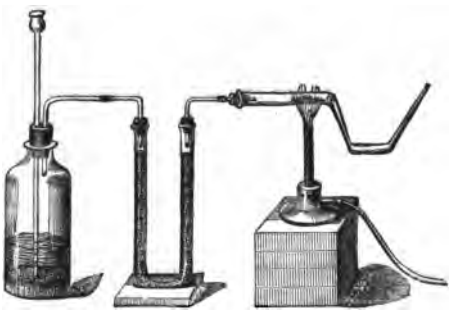


Fig. 27.

length of half-inch combustion tube at two points, and drawing it sideways in opposite directions.

Water will be formed, and will condense in the lowest part of the tube beyond the flame, while beads of metallic lead will remain in the heated portion. The reaction may be represented by the equation

$$PbO + H_2 = Pb + H_2O$$

if the 207 parts of lead united to the 16 parts of oxygen be represented by Pb.

For the oxide of lead used in this experiment, the oxide of most of the heavy metals may be substituted with a similar

* Do not forget to expel all air from the apparatus before applying heat.

result, *i.e.*, the hydrogen will take away their oxygen, and so *reduce* the metal from its oxide. Hydrogen is, therefore, called a reducing agent. Hydrogen reduces many chlorides and some sulphides as well as oxides.

48. Submit the oxide of iron formed in the experiment described in § 35 to the action of hydrogen in this same way. It will be reduced, as will be shown by the formation of water, *i.e.*, an action exactly the reverse of that which occurred on its formation takes place; that was

$$3\,Fe + 4\,H_2O = Fe_3O_4 + H_8$$

this is

$$Fe_3O_4 + H_8 = 3\,Fe + 4\,H_2O.$$

If hydrogen will thus reduce iron oxide, how is it possible that it should be liberated from water by iron? The conditions in the two experiments are different. In the first case there is a rapid current of steam which sweeps the hydrogen away as fast as it is formed, and before it has time to react on the iron oxide made when it was liberated, and in the second there is a current of hydrogen which carries off the water vapour, and prevents the re-formation of iron oxide.

CHAPTER V.

WATER.

49. HAVING shown that water is not an element, but that it consists of oxygen and hydrogen, it remains to show in what proportions these two elements are united. This may be done in several ways, one only being sufficiently simple for performance by a beginner. I will, however, describe the others, as they afford good illustrations of the methods employed in determining such points, and at the same time exhibit some of the properties of hydrogen and other things employed.

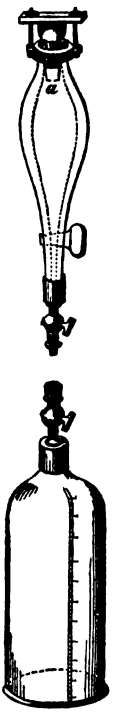


Fig. 28.

1st. The synthetical method first employed by Cavendish, by which the composition of water was originally determined with accuracy. This method consists in making a mixture of pure oxygen and hydrogen in a bell jar, fig. 28, furnished with a brass cap and stopcock, allowing some of the mixture to flow into a very strong glass vessel which has been previously exhausted by the air-pump, through the stopper of which two platinum wires pass and nearly meet inside; passing an electric spark between those wires to cause the two gases to combine; then examining the residual gas to see whether it be oxygen or hydrogen that is in excess; adding more of the gas which is in deficiency to the stock of mixed gases in the bell jar, then exploding another portion of the mixture, and so on, until it is found that the two

gases combine completely without leaving an excess of either. Having found in this way that for every measure of oxygen used, there must be two measures of hydrogen, a mixture of some quantity of these gases in these proportions may be prepared, and then exploded in successive small portions in the pear-shaped vessel. In this way water may be prepared in quantity sufficient to recognise its properties.

50. 2ndly. By a modification of this process, which dispenses with the necessity of the cumbrous and expensive apparatus described above, and is therefore adapted for actual practice. Fill an accurately graduated tube about a foot in length and ·75 inch internal diameter, and closed at one end, with mercury, and stand it mouth downwards in a tall narrow jar of the same metal. About half fill it with dry hydrogen, sink the tube in the mercury till the metal is at the same level inside and outside, and note accurately the volume of the gas.* Fill two-thirds of the remaining space with pure oxygen, and again note the volume of the mixed gases, taking the same precaution as before. Pass up into the mixed gases a little ball of mixed clay and spongy platinum fixed at the end of an iron wire. Under the influence of the platinum the two gases will immediately begin to unite, and the mercury will rise in the tube. Allow the little ball to remain in the gas as long as any decrease of volume can be observed to take place. When the action ceases, withdraw the ball and measure the residual gas, and then test it to see whether it be oxygen or hydrogen. Suppose now the tube used was divided into 100 equal parts, and that there were 53 measures of hydrogen originally introduced, and 24 measures of oxygen, then 77 measures would be the total volume of the mixed gases. After combination we should find 5 measures of hydrogen left unacted on, but no oxygen; now the diminution of volume equals 72 measures,† of which 24 are due to the oxygen, and the other 48 to hydro-

* Avoid touching the tube with the hands or the heat will cause the gas to occupy a volume greater than its real one.

† The water produced occupies only $\frac{1}{1000}$ of the bulk of the gases from which it is formed, and may therefore be neglected.

gen, *i.e.*, every measure of oxygen has combined with two of hydrogen. This experiment may also be performed by exploding the mixed gases by an electric spark passed between two platinum wires fused into the upper end of the tube, which must be strong and only partly filled before being pressed strongly against a caoutchouc pad at the bottom of the mercury. The arrangement of the apparatus for this form of the experiment is shown in fig. 29. The same precautions must be observed in measuring the gas as in the case of analysing air. § 30.

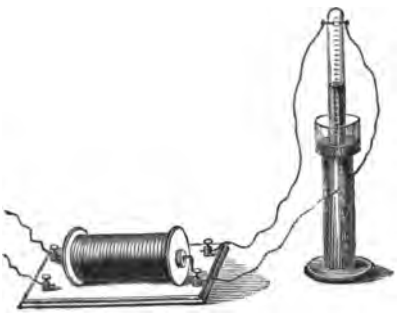


Fig. 29.

The little balls mentioned are made by mixing "spongy platinum" (prepared by igniting ammonio-chloride of platinum [see ammonia tests for]) with three times its weight of pipe clay softened with water, and rolling the mass so obtained into pellets the size of peas round the hooked ends of pieces of steel wire—then drying the balls thoroughly before the fire and igniting them in the flame of a lamp.

Platinum, whether in the form of leaf, wire, or in powder, possesses the power of bringing about the combination at ordinary temperatures of many bodies which will not unite otherwise, except at a red heat or under the influence of the electric spark. This is so in the case of oxygen and hydrogen, which may be kept for any length of time in the same vessel without combining, but begin to unite directly they are brought into contact with a clean surface of platinum. As the surface of foil or wire is small, the action is very slow if the metal be used in these forms, whereas the sponge exposes an enormous surface, and produces a correspondingly rapid combination. As before stated, all chemical combination is attended by rise of temperature, so in this case if you were to allow a little pellet of pure spongy platinum to rise through the mercury

in the tube, and so come in contact with the mixed gases; combination would be immediately set up between those particles of gas in contact with the platinum, heat would be evolved, raise the temperature of the platinum, which then would act more energetically than before, and so be heated more and more until it became red hot and caused the remaining gas to explode; as this accident would probably destroy the tube and spill the mercury, it is necessary to add the clay to moderate the action.

51. It may here be remarked, that though heat brings about the combination of oxygen and hydrogen, it is also capable of decomposing water. When a little ball of white hot platinum is plunged below the mouth of a test tube filled with and inverted in water, a considerable volume of steam is formed by the heat, and that steam contains a small quantity of mixed oxygen and hydrogen in a free state. The mixed gases collect at the upper part of the tube. The same decomposition occurs when steam is passed through a tube of white hot platinum, but in both cases the quantity of steam decomposed bears a very minute proportion to that which remains unaltered.

52. 3rdly. By an analytical process, which is, however, not so satisfactory as the synthetical ones.

Take a wide-mouthed bottle capable of holding about a pint; cut off (see manipulations) about half its height, leaving the neck on the uninjured part; fit an india-rubber plug to the mouth. Attach two slips of platinum foil to two short stout wires of the same metal, and pass these wires water-tight through the plug. Cover the plates with water acidulated with oil of vitriol, and connect each by means of a binding screw with one terminal of a galvanic battery of five or six pairs of plates. As the zinc of the battery is positive as compared with the copper, silver, or platinum used as the other element, the pole in connection with it will be negative, and will attract to itself the positive element of the water, *i.e.*, the hydrogen, while the oxygen, being negative, will be attracted to the positive pole which is connected with the copper, &c., of the battery. As neither gas can combine with the platinum poles, they will both be given off in the free state, and may be collected in two graduated tubes filled with acidulated water and supported over the little plates.

In performing this experiment, it will be observed that one gas collects twice as fast as the other, and that when its tube is quite filled, the other is only half so. Hydrogen is, of course, the more abundant one, as may be shown by testing with a

match. As oxygen is slightly more soluble in water than hydrogen, and as, moreover, it has a tendency to combine with water and form binoxide of hydrogen, under the circumstances of the experiment, we always find it in rather less proportion than required by theory.

53. The determination of the composition of water by weight is one which an apt pupil may make in a rough manner, if he follows with care the directions given.

Fig. 30.

To an apparatus for evolving hydrogen, large enough to give a steady long-continued supply of gas, attach the purifying series of tubes mentioned in § 29, with the addition of a washing bottle containing sulphuric acid, to ensure the perfect drying of the gas. Then heat *about* half an ounce of cupric oxide, Cu O, in a porcelain crucible over a lamp until it is nearly red hot, and therefore thoroughly dry. While it is still hot, scoop it up with the wider end of the bulbed tube of infusible glass, represented in the margin, and immediately close both ends of this tube with caps of india-rubber tube, plugged at one end with bits of glass rod. Shake all the oxide into the bulb, and take special care that none remains in the bent limb. Let the tube and its contents cool thoroughly, which will take at least half an hour, and then weigh caps and all as accurately as the balance at your disposal will admit, and note the weights. (A good pair of apothecary's scales will serve, if furnished with a good set of weights.) While the last tube is cooling, prepare the next part of the apparatus, which consists of a U tube, about three inches long in each leg, fitted with two caoutchouc corks, the one bored to receive the bent arm of the bulbed tube, and the other to take a bit of quill tube bent twice at right angles. This last leads to a second smaller U tube also provided with india-rubber corks. The first U tube is to have a bit of wire-gauze pushed down the limb which will be furthest from the bulbed tube, nearly to the bend, and then the space above the wire-gauze filled with coarse fragments of calcic chloride ($Ca Cl_2$). The second U tube is to be filled with finer fragments of calcic chloride, and connected with the first. The openings of both extremities are now to be closed, the one with a plug of glass rod, and the other with a cap, to prevent absorption of moisture from the air; the whole cleaned outside and put by for a short time to cool after the handling. When quite cold take the weight carefully, and make a note of it. Now attach the wide end of the weighed bulb tube to the apparatus

for evolving hydrogen, and insert the bent limb (which should be slightly tapered) in the hole of the cork of the first U tube, so that it projects half an inch on the inside. Lay aside all the caps and plugs in a dry place, and in such order that you will know which is which. Set up a steady current of hydrogen, and when ALL *the air* is expelled from the apparatus (which will not be in less than an hour, as there must not be a *trace* of air left behind, as the oxygen of it would form water with the hydrogen), apply heat to the bulb containing the oxide of copper, while a slow current of hydrogen still passes. The reducing action, explained in § 32, will be shortly set up, and the water formed will pass on into the two U tubes beyond. Some of this water will condense in the liquid form in the bend of the first tube, and the rest will be absorbed by the chloride of calcium, while only the excess of dry hydrogen will escape from the last opening. Continue to pass hydrogen, and to heat the cupric oxide until the reduction seems complete; then allow the whole to cool while a current of hydrogen is kept up. Detach the various parts which were before weighed, and weigh them again, after having sucked a little dry air through them and replaced the caps, &c., which they were before furnished with.*

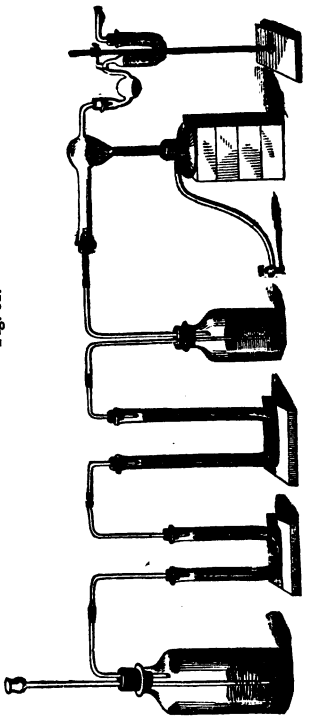


Fig. 31.

Now the oxide of copper, having lost some or all of its oxygen, must weigh less than it did before. Note this loss of weight, and call it oxygen. The two terminal U tubes now contain the

* A simpler absorption apparatus is shown in the figure. The bulb serves to retain most of the water formed, and the calcic chloride beyond catches the rest.

water formed by the union of hydrogen with that oxygen, and their increase in weight shows how much water has been formed. Deduct the weight of oxygen which you have found to be used from the weight of the water formed, and you evidently have the weight of the hydrogen which has united with that oxygen.

If the experiment has been conducted with sufficient care, it will be found that the hydrogen is exactly one-eighth the weight of the oxygen, and therefore forms one-ninth of the weight of water.

54. From the proved composition of water by volume, the composition by weight can be deduced; for since two volumes of hydrogen unite with one of oxygen, and oxygen is sixteen times as heavy as hydrogen, bulk for bulk, water must contain 8 parts oxygen to 1 of hydrogen.

55. The constancy of this ratio (and that between the weights of the elements composing any given compound), together with other facts not yet alluded to, is explained in a simple and satisfactory manner by the "Atomic Theory," which assumes that matter is composed of indivisible particles or "atoms" of indefinite minuteness, having certain proportional weights, as compared with one another, and capable of uniting one with another. Hydrogen, which combines in the smallest proportion of any known element with other bodies, is supposed to have the lightest atoms, and so we say its atomic weight is 1.*

56. We have proved that in water 1 part of hydrogen is always united with 8 parts by weight of oxygen; and if we knew nothing more about water than that, we should be justified in considering water to be formed by the union of one atom of oxygen weighing eight, with one of hydrogen weighing one, and might represent it either by the symbols H O representing those weights, or by ⓗⓞ, which pictures two particles joined together. But if sodium be thrown into water,

* The atomic weight of an element may be defined as the smallest weight of that element which can exist in combination.

it turns out hydrogen and takes its place; if the strongly *alkaline* (see § 217) solution so obtained be evaporated to dryness, and heated to redness, a mass having the composition represented by Na H O (in which Na = 23, H = 1, and O = 16) is obtained. By this we see that the action of the sodium was to turn out *half* the hydrogen of a given quantity of water; therefore that portion of water contained at least two atoms of this element, for a single atom would, of course, by its definition, be indivisible; but the new compound, Na H O, contains the same weight of oxygen as the original water entering into the reaction, and that oxygen does not become divided by half going off with the remaining hydrogen as water, even when the mass is raised to a red heat. If, while the sodic hydrate (Na H O) is fused, more sodium is thrown into it, the second atom of hydrogen is expelled, and we obtain the body, anhydrous soda, or sodic oxide, Na_2 O, by a reaction represented by

$$Na\,H\,O + Na = Na_2\,O + H.$$

In these experiments we, therefore, seem to find proof that the smallest portion of water which can exist in a free state (*i.e.*, one molecule) contains two atoms of hydrogen and one only of oxygen, for we can *divide the one, and not the other.* Therefore we represent water as H_2 O, in which O stands for an atom of oxygen weighing 16.

57. Granting the truth of the Atomic Theory, it is, of course, easy to understand why any given quantity of a compound always contains its constituent elements in the same proportions, because each molecule* is only a reproduction of the rest. Thus, if we represent one molecule of water as (H)(O)(H), every other molecule will be formed in the same manner, and a gross aggregate of any number of them will obviously contain twice as many atoms of hydrogen as of oxygen, and therefore will consist of $\frac{1}{9}$ hydrogen and $\frac{8}{9}$ oxygen. Of course, the

* The smallest quantity of a compound or element which can exist in a free state.

molecular weight of any compound must be equal to the sum of the weights of the elements composing it.

57*a*. The symbol of any element stands always for a single atomic weight of that element. Thus, Ag does not mean an indefinite quantity of silver, but means 108 parts of silver. Likewise Cl means 35·5 parts of chlorine, and therefore Ag Cl will stand for 143·5 parts of argentic chloride (chloride of silver). Two, three, or more atoms of a given element are represented by attaching a little figure to the right of its symbol, when it affects only that symbol, as in $Mn\ O_2$, which means *one* atom of manganese and *two* of oxygen; or by putting a large figure to the left of the symbol, when it multiplies *all the symbols up to the next sign*, as in $3Mn\ O_2 = O_2 + Mn_3\ O_4$, which means that three times $Mn\ O_2$ yield two atoms of oxygen and one molecule of manganoso-manganic oxide, consisting of three atoms of manganese (55×3) and four atoms (16×4) of oxygen.

58. As it has been before remarked, the spaces occupied by quantities of the elementary gases oxygen, hydrogen, and nitrogen, represented by what we will now call their atomic weights, are equal under equal circumstances of temperature and pressure (1 grain of hydrogen, 16 grains of oxygen, and 14 grains of nitrogen, all occupying the volume of 44·4 cubic inches); or 1 gramme of hydrogen, 16 grammes of oxygen, and 14 grammes of nitrogen, occupy 11·2 litres at 0° centigrade, and 760 millemetres barometer pressure. What is true of these is also true of other elementary gases, with one or two exceptions; we are, therefore, led to consider that equal volumes of these elements contain the same number of atoms in each case. These volumes may, of course, be taken on any scale, as the *proportion* between the weight and volume will remain the same. For instance, if we take a cubic yard, or cubic metre, as our standard of bulk, and if there be in this space as many atoms of oxygen as of hydrogen, and if the atom of oxygen is sixteen times as heavy as the atom of hydrogen, it follows that a cubic yard or metre of oxygen will weigh sixteen times as much as the same bulk of hydrogen. Moreover, as all gases expand at the same rate under

the influence of heat, and are affected in the same manner by change of pressure, the proportions between the weights of equal volumes of various elementary gases will be the proportions between their atomic weights whatever the temperature and pressure at which the comparison is made; always providing they are all under the *same* conditions.

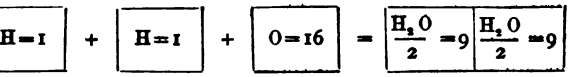
59. Turning now to water, our first example of a compound body, it is obvious that while it is a liquid, the volume occupied by its molecules is not comparable to the volume of an atom of hydrogen which is a gas; but by heat water is converted into a gas (steam), and then the weight of a given volume of it may be compared to that of an equal volume of hydrogen at the same temperature. By experiment, the proportion is found to be—

Steam : Hydrogen (at same temp.) :: 9 : 1.

i.e., any given volume of steam will weigh nine times as much as the same volume of hydrogen at the same temperature. (N.B. In practice the temperature of the steam has to be about 30° centigrade above the temperature of water boiling under the pressure at which the experiment is performed.) This fact is expressed by saying that the vapour density of water is nine, hydrogen being unity. It has been agreed that the molecular weight of water is eighteen, and that one volume of its vapour only weighs nine times as much as one volume of hydrogen; therefore one volume of water vapour is only half a molecule, or the molecule occupies two volumes.

60. Again, if a mixture of exactly 2 volumes of hydrogen and 1 volume of oxygen be made in a eudiometer, provided with platinum wires (like that in fig. 29), so as to fill about one-fourth of its capacity, then raised to a temperature considerably above the boiling point of water, and exploded by the passage of an electric spark, the water which is formed will remain in a gaseous state, and will occupy *two-thirds* of the space which the *mixed* gases occupied at the same temperature at which the volume of the steam is observed. This may be represented

thus :—Equal squares, or other figures, being taken to represent equal volumes of the gases, these volumes having weights proportional to their atomic weights,



That is, three volumes of *mixed* gases condense on combination into two volumes of the compound; and two volumes of water vapour contain two volumes of hydrogen and one volume of oxygen, or, steam contains its own volume of hydrogen and half its volume of oxygen.

The mode of performance of the above very important experiment is not given, because it requires more expensive and elaborate apparatus than is usually to be found in a school. A full and accurate description of the most convenient form of the experiment is to be found in Hofmann's "Modern Chemistry."

61. In like manner we find that all other *compound* gases and vapours (with a few exceptions) are two-volume vapours, *i.e.*, the molecular weight of any one of them takes up twice the space of an atomic weight of hydrogen (expressed in the same units), at the same temperature.

62. Here we are met by the difficulty that if we wish to compare gaseous elements and compounds one with the other, we are dealing with dissimilar standards; the "atom" in the one case, and the "molecule" in the other. This is met by taking the molecular weights in all cases, both for elements and compounds, as the measure of the quantities of bodies with which we have to deal; thus the quantity of hydrogen which we compare to the molecule of water H_2O, is not one volume represented by H, but two volumes or one molecule H_2; and so with other elements. There are other reasons besides this one of convenience for taking the molecule of an element as representing the smallest quantity of it with which we have to deal; these reasons cannot be given here, but for the future, all re-actions in which an element is used, or evolved, will be so written as to deal only with molecular weights of those elements.

63. Water never occurs quite pure in nature, but always holds in solution either gaseous or saline impurities. These latter are so little volatile, that when water containing them is converted into vapour, they are left behind; a fact which is taken advantage of in the laboratory to prepare pure water by distillation. The heat of the sun converts the water of seas, lakes, and rivers, into vapour, which being lighter than an equal bulk of air, rises, until it comes into a region cold enough to cause its loss of the truly gaseous state, and to make it assume that form (whatever it is), which it has in clouds, mists, or fog. The water which, so long as it retains the form of vapour, may be considered pure, is by the loss of heat converted into liquid water, which descends through the air in the form of rain, absorbing in its fall some of each of the gases found in the atmosphere. Therefore, if we collect rain water in clean vessels in the open country, we shall find it to consist of water holding in solution, *free* oxygen, nitrogen, and carbonic acid, together with *very* minute traces of ammonia and nitric acid. The presence of the first-named three can be shown by boiling them out, as detailed in § 22, absorbing the carbonic acid by potash, and the oxygen by phosphorus. This solution of gases is possessed of even greater solvent powers than pure water, so that in percolating through the various strata on the earth's surface, it dissolves some things which would not be taken up by water itself. What things are dissolved depends, of course, on what substances the strata through which it passes contain. If the water meets beds of rock salt, or beds containing much salt (chloride of sodium), it will issue from the spring or well highly charged with this very soluble body, but if it only pass through siliceous sand, which is very insoluble, it will emerge almost as pure as it entered. In by far the greater number of localities, the water in its passage through the earth will meet with some common salt, sulphates of lime and magnesia, carbonate of soda, soluble silica, and lastly, abundance of carbonate of lime. All these bodies, except the last, are more or less soluble in *water*, and even that is, only to so slight an extent, that the

quantity might be disregarded did not the carbonic acid present in the water enable it to dissolve a much larger quantity of the calcic carbonate than it otherwise could. That spring water does actually contain these impurities may be shown—

By evaporating to dryness a portion of it in a clean basin and examining the residue. That the carbonate of lime in the water is held in solution by aid of carbonic acid, may be shown by simply boiling some of the water in a flask to expel *free* carbonic acid, when the carbonate of lime, which was held in solution by it, will be deposited on the sides as a thin crust.

The presence of soluble sulphates is shown by adding baric chloride to the water acidulated with hydric chloride (hydrochloric acid), when a slight precipitate of the insoluble baric sulphate will be formed. Chlorides are detected by the formation of a white precipitate of silver chloride, when silver nitrate and hydric nitrate are added to the water.

64. Water holding lime and magnesia salts in solution is what is called "hard," because it decomposes soap to form an insoluble lime soap, which grates on the hands.

The hardness which is due to dissolved calcic carbonate can be got rid of by boiling, as explained above; it is, therefore, called temporary hardness—that due to calcic sulphate, which is not removed by boiling, is called permanent hardness.

The hardness of water is estimated by the amount of soap it will destroy. A water, which will decompose as much soap as a solution of one, two, three, &c. grains of calcic carbonate in 100,000 grains of water will, is said to be of one, two, three, &c. degrees of hardness.

Spring water, which contains iron, is called "chalybeate;" that which holds sulphuretted hydrogen in solution, "sulphuretted," or "hepatic."

River water consists of spring water, plus that derived from the surface drainage of land; it will, therefore, contain the same impurities, and some additional ones, the most notable being organic matter, *i.e.*, matter derived from the decay of organised beings, animal or vegetable. The water of shallow wells is also commonly found to be impregnated with this dangerous filth. The ocean is the ultimate receptacle of nearly all river water.

From its surface, the heat of the sun is constantly removing enormous bodies of pure water (which again returns in the form of rivers, &c., charged with fresh supplies of saline matter), leaving behind the salts contained in it; therefore, they must be constantly accumulating, and the sea-water becoming thereby salter and salter.

The water supplied to London contains on an average about 18 grains of total solid impurity in a gallon (*i.e.*, 70,000 grains).

Sea water contains about 2470 grains per gallon, or 3·5 per cent. Of this large quantity, 1890 grains are common salt (chloride of sodium).

65. Sea and other very impure water requires to be distilled before use for most purposes. This is effected in large copper or

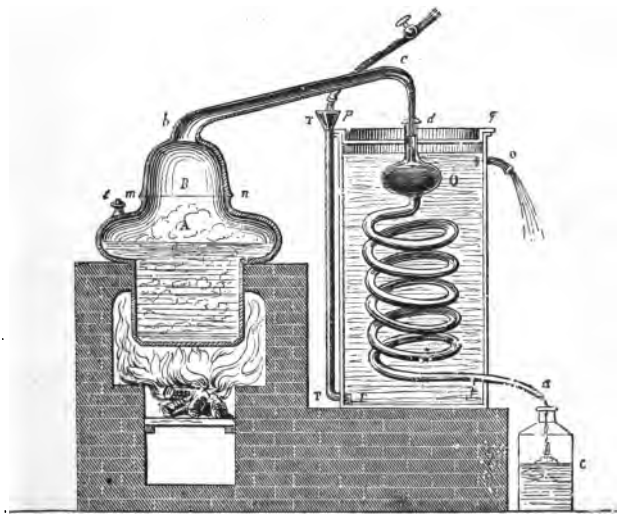


Fig. 32.

iron boilers, provided with a long neck of tin-lined tubing, coiled into spirals, and immersed in often-renewed cold water. The water which condenses is nearly pure, and serves for laboratory

use, but is too insipid to serve well as a drink, because of the absence of dissolved gases. By filtering it through animal charcoal, it dissolves air, &c., and the mawkishness is removed; a fact which is now taken advantage of in most ocean-going steamers.

66. The solvent powers of water will be best discussed under the head of individual bodies, it being only remarked here, that most solids are more soluble in warm water than in cold, and all gases less so. The other physical properties of water, such as its abnormal behaviour under the influence of heat, must be left to works professedly treating on physics.

67. A cubic inch of distilled water at 60° Fahr. (15·5 centigrade), weighs 252·456 grains. A gallon = 10 lbs. avoirdupois = 70,000 grains. A cubic centimetre of distilled water at 4° centigrade weighs 1 gramme; ∴ a cubic decimetre (one litre), which = 1000 cubic centimetres, weighs 1000 grammes, or 1 kilogramme.

68**. One other compound of oxygen and hydrogen is known besides water; it is peroxide or binoxide of hydrogen, H_2O_2, sometimes called oxygenated water. It is prepared by acting on binoxide of barium, BaO_2, by dilute hydric chloride, $BaO_2 + (HCl)_2 = BaCl_2 + H_2O_2$. It has never been obtained in a pure state, but only as a solution in water. It is a very powerful oxidising agent, as it parts with one atom of oxygen with the utmost readiness. Its chief interest arises from considering it as being the free form of that part of metallic hydrates which corresponds to the chlorine of the chlorides.

Free chlorine	(Cl Cl),	Potassic chloride, KCl,	Cupric chloride, $CuCl_2$
Free peroxide of hydrogen, hydroxyl	(HO HO),	,, hydrate, K(HO)	,, hydrate, $Cu(HO)_2$

QUESTIONS ON CHAPTERS IV. AND V.

1. How can it be proved that water is not an element, (*a*) analytically, (*b*) synthetically?

2. How can hydrogen be prepared from hydric sulphate, H_2SO_4? What weight of hydrogen will 10 grammes of zinc liberate from dilute hydric sulphate?—*Ans.* 0·3077 nearly.

3. If iron be substituted for zinc, how much hydrogen will be given off?—*Ans.* 0·357 grammes.

4. What weight of zinc must be added to acidulated water, to liberate 5 grains of hydrogen? (Zn = 65.)—162·5 grains.

5. In what sense is Fe equal to Zn, and Fe or Zn to H_2?

6. What weight of iron is needed to prepare 35 grains of hydrogen from hydrochloric acid?—*Ans.* 980 grains.

7. What weight of hydrogen could I obtain from 70 grains of water by the action of sodium?—*Ans.* 7·7 grains.

8. What experiments serve to illustrate the lightness of hydrogen?

9. What do you mean by "*diffusion*?"—What relation does the rate of diffusion of a gas bear to its density?

10. What is formed when hydrogen burns?

11. Explain why a jet of pure hydrogen burns quietly in the air, while a mixture of the two bodies explodes on being lighted?

12. What is meant by calling hydrogen a reducing agent?

13. Quote and explain experiments illustrative of the reducing power of hydrogen.

14. If 223 grains of plumbic oxide (PbO) be heated in hydrogen, what weight of water will be formed? (Pb = 207.)—*Ans.* 18 grains.

15. What is the composition of water by volume?—How could the composition of water by volume be shown?

16. How many grammes of water would be formed if 100 grammes of cupric oxide lost 20 grammes' weight by heating in hydrogen?—*Ans.* 22·5 grammes.

17. (*a*) What is the composition of water by weight and by volume? (*b*) What weight and what volume of the inflammable constituent could be obtained from 85 grammes of it if completely decomposed?—*Ans.* 9.4 grammes, 105·7 litres.

18. Describe in full the method of determining the composition of water by weight?

19. What are the commonest impurities of spring water?

20. Give an explanation of the saltness of the ocean, and say what that saltness is caused by?

21. How can pure water be prepared from sea water, and how rendered fit for drinking?

22. (*a*) What is the difference between "hard" and "soft" water? (*b*) To what is "*permanent*" hardness due? (*c*) How can water be purified?

23. What do you mean by saying that a given water has ten degrees of hardness?

24. What weight of oxygen is contained in 5 grammes of water?—*Ans.* 4⅔ grammes.

25. What volume (in cubic centimetres) will 0·357 grammes of hydrogen occupy at the normal pressure and temperature?—*Ans.* 3998·4 cubic centimetres.

26. What is the weight of 100 cubic centimetres of hydrogen ?*—*Ans.* ·008928 grammes.

27. Calculate the specific gravity of hydrogen (air being 1).

28. If ten grains of hydrogen were passed over an excess of red-hot oxide of copper, (*a*) what weight of water would be formed ; (*b*) and what loss of weight would the oxide of copper undergo ?—*Ans.* Water formed =90 grains. Loss of weight of oxide of copper=80 grains.

29. What hypothesis enables us to explain the constancy of composition of given compounds ?

30. If a mixture of 28 cubic centimetres of hydrogen and 14 cubic centimetres of oxygen at 150° centigrade be exploded, what volume of steam (at 150° centigrade) will be formed ?—*Ans.* 28 cubic centimetres.

31. If 25 cubic centimetres of hydrogen be mixed with 11 cubic centimetres of oxygen at 150° centigrade, and the mixture exploded, what volume of gas will be left at the initial temperate ? What will the residual gas consist of ?—*Ans.* 22 cubic centimetres of steam,

3 cubic centimetres of hydrogen,

25 mixed gas.

32. What volume of hydrogen is contained in 365 cubic centimetres of steam ?—*Ans.* 365 cubic centimetres.

33. What volume and weight of oxygen is required to burn 700 cubic centimetres of hydrogen ?—*Ans.* 350 cubic centimetres of oxygen which weigh 0·50 gramme.

* See foot note, p. 14.

CHAPTER VI.

CHLORINE AND ITS COMPOUNDS.

69. HAVING acquired some insight into the nature of chemistry, the processes of investigation, and the use of formulæ, by the study of such well-known substances as air and water, we will now proceed by a somewhat different method, and treat of the remaining elements included in our scheme in more philosophical order. And firstly, we will take those elements which combine with hydrogen, atom for atom. These are—chlorine, bromine, iodine, and fluorine.

CHLORINE.—Symbol Cl, Atomic weight 35·5.

Combining Vol. 1, or $\boxed{35{\cdot}5}$, $\left.\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right\}$ = 2 vol. = 71.*

CHLORINE never occurs free, naturally, but always in combination with some metal or other. The commonest chloride is that of sodium (Na Cl), which in the form of sea salt and rock salt is known to exist in enormous quantities; potassic chloride (K Cl) is found in sea water and also in some mineral deposits, and, therefore, also in some springs. Magnesic and calcic chlorides are likewise not uncommon, but the chlorides of the heavy metals,—silver, copper, &c., are comparatively rare.

70. The hydrogen compound—hydric chloride, or hydrochloric acid, is the body from which free chlorine is always prepared. To obtain the element it is only necessary to remove the hydrogen; an object which can be attained by the use of

* The reason for giving the *volume* in the duplicate as well as the single form in this and subsequent cases, will be seen by reference to §§ 60 and 62.

almost any powerful oxidising agent which will give up oxygen to *burn* the hydrogen of the hydric chloride. If the chlorine is wanted in a pure state, no other gas must be made at the same time; we therefore choose some body which, while containing plenty of available oxygen, does not form any volatile compounds, under the conditions of the experiment. Manganic dioxide (binoxide of manganese, peroxide of manganese, black oxide of manganese) $Mn O_2$ is eminently adapted to our purpose, for when added to hydric chloride, the two atoms of oxygen in it unite with four atoms of hydrogen in four molecules of the chloride, and the manganese with the four chlorine, thus—

$$Mn O_2 + 4H Cl = 2H_2O + Mn Cl_4.$$

The manganic tetrachloride, as soon as formed, begins to split up into chlorine on the one hand, and manganous chloride, $Mn Cl_2$, on the other.

$$Mn Cl_4 = Mn Cl_2 + Cl_2.$$

The two stages of the reaction may be merged in one equation—

$$Mn O_2 + 4H Cl = 2H_2O + Mn Cl_2 + Cl_2,$$

which represents in a concise form the results of experiment.

71. The quantity of manganic dioxide represented by $Mn O_2$ is 55 parts (grammes, grains, ounces, or tons) of manganese united to 16×2 parts of oxygen, *i.e.*, in all 87 parts. $4H Cl$ stands for four times the quantity of hydric chloride represented by $H Cl$, which is 36·5. So the equation states that if 87 grammes (grains, &c. &c.) of manganic dioxide be acted on by 146 grammes (&c.) of hydric chloride, there will be obtained 36 grammes (&c.) of water ($2H_2O = 2(2 + 16)$), 126 grammes (&c.) of manganous chloride ($Mn Cl_2 = 55 + 2(35{\cdot}5)$) and 71 grammes (&c.) of free chlorine.

72. This reaction, like most others, is accelerated by heat. The apparatus employed is represented in the figure, and the construction of its parts explained under the head of Apparatus.

It is very necessary that all the joints should be *quite* air-tight, as chlorine is a powerfully irritating and corrosive gas.

Put three or four ounces of the manganic dioxide in the generating flask; add about four times its weight of the strongest "hydrochloric acid" of commerce (the yellow impure body serves as well as the best), and shake well together, replace the cork, fill the bend and half the bulb of the safety tube with the same liquid, connect the exit tube with the long descending tube of the washing bottle by a few inches of vulcanized india-rubber tubing, and apply a very gentle heat. The gas will come off rapidly and regularly, pass through the water in the washing bottle, whereby it will

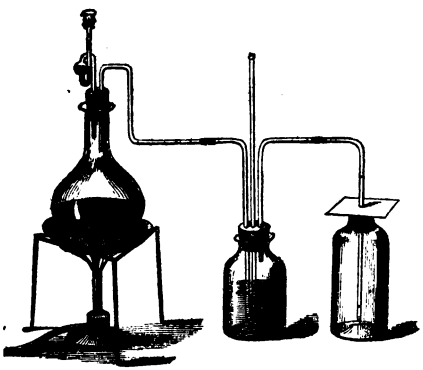


Fig. 33.

be freed from vapour of hydric chloride, and it can then be collected either by downward displacement of air, as shown in the figure, or over *hot salt water* in the pneumatic trough. If for any purpose the gas is required in a dry state, it may be passed through an additional bottle containing fragments of calcic chloride ($Ca\,Cl_2$), or pumice-stone soaked in oil of vitriol ($H_2\,SO_4$), both being bodies which eagerly absorb water, but have no action on the chlorine itself.

Perform the experiments with chlorine in the open air, or in the draught of a fire-place; even the evolution apparatus should be so arranged that if it breaks, the escaped gas shall be immediately carried away from the operator.

73. Chlorine is sometimes made by acting on a mixture of common salt ($Na\,Cl$) and binoxide of manganese ($Mn\,O_2$), by hydric sulphate ($H_2\,SO_4$) (oil of vitriol) in the apparatus just described; the action may be repre-

sented as consisting in, first, the formation of hydric chloride (HCl) by the action of the hydric sulphate on the salt,

$$NaCl + H_2SO_4 = NaHSO_4 + HCl,$$

and the subsequent action of this hydric chloride on the manganic dioxide present. The complete reaction being

$$2NaCl + 3H_2SO_4 + MnO_2 = 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2.$$

It will be observed that there is no manganous chloride here formed, the reason being that when made it is acted on by the excess of hydric sulphate in such a manner as to form manganous sulphate and hydric chloride,

$$MnCl_2 + H_2SO_4 = MnSO_4 + 2HCl,$$

which then acts on another portion of the manganic dioxide, as before.

74. The gas will be observed to be of a yellowish-green colour; a circumstance which will enable the experimenter to mark the progress of filling a vessel with it by displacement. Furthermore, it has a very strong, irritating, and characteristic odour, which is sure to be noticed, whether wished for or not. Should the operator inhale too much of the gas, he will obtain some relief by breathing a little vapour of ether or alcohol. Ammonia vapour rather increases than allays the pain. The effects of the inhalation of any considerable quantity of chlorine are so serious that the utmost care should be taken to make all parts of the apparatus as tight as possible, and even then, to work in a draught which will carry the escaped gas away. Among the physical properties of the gas, we may notice

75. Its solubility, which may be shown by filling a narrow-mouth stoppered bottle with it, opening the mouth of the bottle under water, admitting a small quantity of that liquid, reclosing the bottle and shaking, then opening the bottle again beneath the water, when more will rush in to supply the place of the gas absorbed. After repeating these operations a few times the bottle will be filled with a solution of chlorine having the characteristic colour and smell of the gas itself.

Also pass a stream of the gas through a second bottle half filled with cold distilled water till the latter has acquired the colour of the gas itself (fig. 34). Preserve this solution in a well stoppered bottle kept in a dark

place. If the water is really saturated, *i.e.*, if it contains as much chlorine as it can dissolve, it will hold in solution three times its own volume.

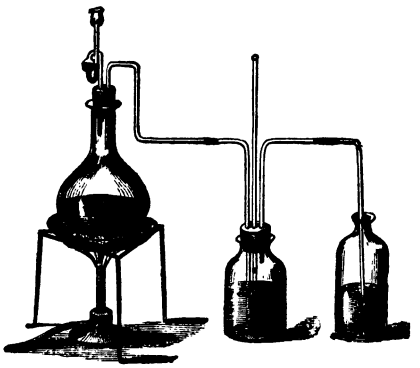


Fig. 34.

76. The standard (or absolute) volume (11·2 litres) of chlorine, weighs 35·5 grammes, the conditions being the same as those under which the same volume of hydrogen weighs 1 gramme, therefore it is heavier than hydrogen, as $\frac{35·5}{1}$, than oxygen as $\frac{35·5}{16}$, than nitrogen as $\frac{35·5}{14}$, and than air as $\frac{35·5}{14·4}$.

77. When chlorine is compressed by a force of four atmospheres (4 × 15lbs. per square inch), at the ordinary temperature, it condenses to a yellow liquid which sinks in water and dissolves but slightly. The liquid chlorine cannot be solidified by cold. Of the chemical properties of chlorine observe—

78. The energy with which it combines directly with hydrogen and the metals may be shown by the following experiments :—

Make a mixture of *equal volumes* of hydrogen and chlorine in a darkened room; decant some of it into a *small, very stout* wide-mouthed bottle, close the ground mouth of this by a greased plate of wood, and then carry it with an opaque cover on into direct sunlight. An immediate explosion results on removing the cover. To another portion of the same mixture apply a light; the same result will follow.

Question. What is the cause of this explosion ?

Fill another larger bottle, having a well ground and greased stopper,

with the same mixture, and expose it to diffused daylight. In time the colour of the chlorine will disappear, because it will unite with the hydrogen to form hydric chloride (HCl), which is colourless. Put away another portion of the mixture in a dark place; even after the lapse of weeks the colour of the chlorine will be visible (if the bottle was perfectly stoppered), showing that the influence of light or heat is required to bring about the union of these two elements.

A very instructive way of trying these experiments is to fill two equal-sized bottles, one with chlorine the other with hydrogen, and to connect them by a piece of narrow glass tube passing through their corks. The two gases will become perfectly mingled in a short time, owing to diffusion (see § 45), even if the heavy chlorine is placed undermost.

Fill two large wide-mouth stoppered bottles (quart size) with dry chlorine, by displacement; let the gas be as little mixed with air as may be, to which end cover the mouth of the bottle with a card having a notch in it for the delivery tube (see fig. 33). Powder a little metallic antimony very fine, then shake some of this powder, from the point of a knife, into one of the jars. As the metal passes through the chlorine it unites with that body with so much energy that heat and light are evolved; in other words, the metal catches fire, chloride of antimony ($SbCl_5$) being formed. The object of powdering the metal is, of course, to give it a great surface, so that the action may be rapid. Into the other jar introduce some leaves of Dutch metal (false gold-leaf, consisting of copper and zinc) at the end of a wire. They immediately burn, forming a mixture of cupric chloride ($CuCl_2$) and zinc chloride ($ZnCl_2$).

To the exit tube of the drying bottle (or U tube) of a chlorine apparatus, attach a two-foot length of three-quarter inch glass tube containing some fragments of a metal, such as iron, copper, tin, &c., at the end next the chlorine supply. Pass a current of the gas and apply a gentle heat if necessary. The metal will be converted into its chloride, which will either remain at the place of its formation or sublime and condense in the colder part of the tube, or pass on with the excess of gas (as in the case of tin), when it may be made to condense by passing it into the U tube surrounded by crushed ice and salt, represented in the margin. In this way very beautiful specimens of metallic chlorides can be made.

Fig. 35.

In this and similar experiments, the excess of chlorine which escapes from the end of the apparatus may be led by a tube into a glass containing slaked lime, stirred up with water, or into spirit of wine (methylated spirit), either of which will absorb the excess of gas and prevent its causing

annoyance; or, better still, use a large washing bottle filled with coke, soaked in a strong solution of soda.

79. Fill a large wide-mouth bottle with chlorine; fix a candle to the end of a wire, and plunge it lighted into the gas. It will be observed that the gas does not itself kindle, but that the candle continues to burn, only with a small red smoky flame, giving off abundance of black smoke, which settles on the sides of the bottle as soot, and also a gas which gives white fumes when it comes into contact with moist air. The candle, supposing it to be paraffin, consists of *carbon* and *hydrogen*, therefore the gases rising from its wick will consist of the same elements. These gaseous hydrocarbons are hot under the conditions of the experiment, and on coming into contact with the chlorine are by it decomposed; their hydrogen combines with the chlorine to form hydric chloride, while their carbon is set free in the form of the before-mentioned soot.

Fig. 36.

Turpentine ($C_{10}H_{16}$) is acted on even in the cold with great rapidity, by chlorine, with accompanying rise of temperature. If the turpentine is poured over a piece of porous paper so as to expose a great surface, and this paper then plunged into a jar of the gas, the whole will soon burst into flame, owing to the energy with which the chlorine unites with the hydrogen of the turpentine. Carbon, as in the preceding experiment, is set free, because under such circumstances it is unable to unite with chlorine.

80. One of the most valuable properties of chlorine is its power of bleaching vegetable and animal colouring matters. To observe this in the most advantageous manner, proceed as follows:

Fill a wide-mouth bottle with dry chlorine, drop a few bits of chloride of calcium into it, close its mouth with a well greased stopper, and allow it to stand, while you dry a strip of blue litmus paper very thoroughly before the fire. Introduce this paper and reclose the bottle. If both gas and paper have been well dried, little or no change will take place in many days, weeks, or even months; but if the stopper be removed and the paper moistened in one spot by a drop of water, the colour at that spot will be immediately discharged.

Indigo, which resists the action of the strongest oil of vitriol, is instantly bleached by chlorine, as can be shown by adding a solution of the latter to one of indigo sulphate. Mineral colours, such as lampblack (used in printing ink) are not affected in the

same way as animal and vegetable ones, for a reason which will be explained further on.

81. The compounds of chlorine are very numerous, the formulæ and names of some of the most important are here given:—

H Cl	Hydric chloride	Hydrochloric acid.
Cl Cl	Chloride of chlorine*	Free chlorine.
I Cl	Iodous chloride	Protochloride of iodine.
$I Cl_3$	Iodic chloride	Terchloride of iodine.
K Cl	Potassic chloride	Chloride of potassium.
Na Cl	Sodic chloride	Chloride of sodium (common salt).
Ag Cl	Argentic chloride	Chloride of silver.
$(NH_4)Cl$	Ammonic chloride	Chloride of ammonium (sal ammoniac).
(CN) Cl	Cyanous chloride	Chloride of cyanogen.

In these bodies we perceive that one atom of chlorine is united with one atom of the other element (or compound radical, *e.g.* (NH_4) or (CN)), so that they all have the same combining power as hydrogen, and are therefore said to be equivalent to one atom of hydrogen, or to be monovalent or monoatomic. The case of iodine will be discussed afterwards.

82.

$O''Cl_2$	Chlorous oxide, anhydrous hypochlorous acid.
$O_3''Cl_2$	Chloric teroxide, anhydrous chlorous acid.
$O_4''Cl_2$	Chloric tetroxide, or peroxide of chlorine.
Ca″Cl	Calcic chloride, or chloride of calcium.
$Ba''Cl_2$	Baric chloride, or chloride of barium.
$Mg''Cl_2$	Magnesic chloride, or chloride of magnesium.
$Mn''Cl_2$	Manganous chloride, or chloride of manganese.
$Zn''Cl_2$	Zinc chloride, or chloride of zinc.
$Fe''Cl_2$	Ferrous chloride, or protochloride of iron.
(Fe'''_2Cl_6)	Ferric chloride, or perchloride or sesqui-chloride of iron.
$Cu''Cl_2$	Cupric chloride, or chloride of copper.
Cu''_2Cl_2	Cuprous chloride, or subchloride of copper.
$Pb''Cl_2$	Plumbic chloride, or chloride of lead.
$Hg''Cl_2$	Mercuric chloride, or corrosive sublimate.
Hg'_2Cl_2	Mercurous chloride, or calomel (subchloride of mercury).
$(CO)''Cl_2$	Chlorocarbonic acid, or chloride of carbonyl (phosgene).
$(C_2H_4)''Cl_2$	Ethylenic chloride, or Dutch liquid.

These elements form compounds with chlorine in which there are two atoms of chlorine to one of the metal, &c. In these cases they are di-valent. Some form more than one compound with chlorine, but the consideration of these cases must be postponed.

* The names marked * are very seldom or never used.

83. $N'''Cl_3$ (?) . Nitric trichloride, terchloride of nitrogen.
$B'''Cl_3$ . . Boric trichloride, terchloride of boron.
$P^{v}Cl_5$ . . Phosphoric chloride (phosphoric pentachloride), pentachloride of phosphorus.
$P'''Cl_3$ . . Phosphorous chloride (phosphoric trichloride), terchloride of phosphorus.
$As'''Cl_3$ . . Arsenious chloride, terchloride of arsenic.
$Sb^{v}Cl_5$ . . Antimonic chloride, pentachloride of antimony.
$Sb'''Cl_3$ . . Antimonious chloride, terchloride of antimony.
$Bi'''Cl_3$ . . Bismuthous chloride, terchloride of bismuth.
$Au'''Cl_3$ . . Auric trichloride, terchloride of gold.
$(PO)'''Cl_3$. Chlorophosphoric acid, phosphoric oxychloride.

These compounds show the elements united to chlorine are either tri- or pentavalent.

84. $C^{iv}Cl_4$ . . Carbonic tetrachloride, or tetrachloride of carbon.
$Si^{iv}Cl_4$ . . Silicic tetrachloride, or tetrachloride of silicon.
$Sn^{iv}Cl_4$ . . Stannic chloride, or tetrachloride of tin.
$Sn''Cl_2$ . . Stannous chloride.
$Pt^{iv}Cl_4$ . . Platinic chloride.
$Pt^{iv}Cl_2$ (?) . Platinous chloride.

These last are tetravalent elements, as their chlorides show. The *valency* of an element is indicated by the small Roman figures on the upper right-hand side of the symbol.

Observe that where the same element unites with chlorine in more than one proportion, the compound having the least chlorine has its name ending in *ous*, while the other terminates in *ic*.

HYDRIC CHLORIDE. HYDROCHLORIC ACID.

$$H\,Cl = 35{\cdot}5 + 1 = 36{\cdot}5 = \boxed{18{\cdot}25}\ \boxed{18{\cdot}25}$$

85. As before shown, chlorine combines directly with hydrogen to form this compound, which is not, however, actually made in this way for use. Common salt, Na Cl, has its sodium replaced by hydrogen by a reaction which is of very general applicability. Hydric sulphate (H_2SO_4) otherwise called sulphuric acid or oil of vitriol, when heated with a metallic chloride re-acts in the manner indicated in the following equations, in which M′ stands for a metal having the same combining

power as hydrogen, and M″ for one the atom of which has twice that power.

$$M' Cl + H_2SO_4 = MH SO_4 + H Cl, \text{ or } \left\{ \begin{array}{c|c} M' & Cl \\ SO_4H & H \end{array} \right.$$

$$M'' Cl_2 + H_2SO_4 = M'' SO_4 + 2 H Cl, \text{ or } \left\{ \begin{array}{c|c} M'' & Cl_2 \\ SO_4 & H_2 \end{array} \right.$$

i.e., the metal of the metallic chloride is exchanged for an *equivalent* quantity of hydrogen, and a metallic sulphate and hydric chloride formed.

In the second forms of these equations, the symbols on the same horizontal line constitute the formulæ of the reacting substances *before* action, and those cut off by the vertical line those of the products.

86. To apply this reaction to the preparation of hydric chloride, place in a flask, similar to that used for making chlorine, half a pound of common salt; then weigh out enough hydric sulphate to react on it completely, according to the equation just given. Pour it into a flask containing a quantity of water equal to half its weight. Cool this mixture (heat is evolved when hydric sulphate and water are mixed), and pour it through the safety funnel on to the salt. The application of a gentle heat will now cause the evolution of hydric chloride, in the form of a gas, which can be conducted into any vessel required.

87. To calculate the quantity of H_2SO_4 required: the equation is

$$Na Cl + H_2SO_4 = Na H SO_4 + H Cl,$$

which states that the quantity of sodic chloride represented by Na Cl requires the quantity of hydric sulphate represented by H_2SO_4. Now Na = 23 and Cl = 35·5 ∴ Na Cl = 58·5: in a like manner S = 32; O_4 = 64 and H_2 = 2 ∴ H_2SO_4 = 98, *i.e.*, 58·5 parts of chloride of sodium require 98 parts of hydric sulphate. To solve the problem above we have only to make a proportion sum of it—

$$58·5 : \text{say } 8 \text{ oz.} :: 98 : x;$$

Or, putting it in another way—

$\because$ 58·5 parts of sodic chloride require 98 of hydric sulphate.

$\therefore$ 1 „ „ „ „ $\frac{98}{58{\cdot}5}$ „ „

$\therefore$ 8 oz. „ „ „ „ $\frac{98}{58{\cdot}5} \times \frac{8}{1}$

88. If only half as much hydric sulphate as indicated above be used, the reaction which takes place is represented by—

$$2\ Na\ Cl + H_2\ SO_4 = Na_2\ SO_4 + 2\ H\ Cl.$$

That is, the whole of the hydrogen of the hydric sulphate is replaced by sodium; but as the body $Na\ H\ SO_4$ is first formed, and as it reacts on the remaining sodic chloride with difficulty, a temperature too high for glass vessels is required. On the manufacturing scale, where iron retorts are used, this proportion of hydric sulphate is better as being more economical.

89. The gas being heavier than air in the proportion of $\frac{36{\cdot}5 \div 2}{14{\cdot}4}$ (because $H\ Cl = 36{\cdot}5 = 2$ vol., 1 standard vol., *i.e.*, 11·2 litres if it weighs 18·25 grammes, and the same vol. of air weighs only 14·4 grammes), may be collected by downward displacement in narrow-mouthed bottles.

Pass the gas as it comes from the generating flask, through a small empty bottle, furnished with an entrance and exit tube, and kept cool (fig. 37), and from thence to the bottom of a dry narrow-mouthed stoppered bottle of about half a pint capacity. After the gas has filled this last it will of course overflow into the surrounding air, and in doing so will give rise to the production of thick white fumes, although it itself is perfectly clear, transparent, and colourless, as will be seen.* Close this bottle with its well-greased stopper and replace it by another; when this one

* The fumes are caused by the gas uniting with the moisture of the air, and forming a body which is so much less volatile that it condenses into minute particles of liquid, such as those which constitute cloud; these intercept and reflect light, and are, therefore, visible.

is full, put another half full of distilled water in its place. These operations must in practice succeed one another without interval,

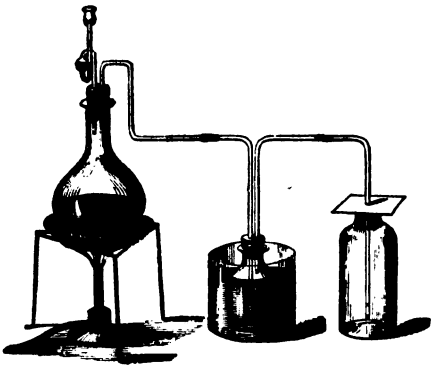


Fig. 37.

to avoid the escape of large quantities of this irritating gas. Observe that the bubbles of gas as they get into the water in the last bottle instantly collapse, and that the liquid gets hot and increases in bulk; allow the gas to continue to pass into the water until no more is absorbed.

90. Examine, in the following manner, the portions of gas first collected.

Into one bottle put a lighted taper at the end of a wire; it will be extinguished; remove the candle and introduce a slip of moistened litmus paper; it will be reddened, but *not bleached*.

Open the mouth of the other bottle under the surface of water; the liquid will rush up into it in so violent a manner, that unless it be held firmly it may be knocked out of the hand and broken. Observe how much more readily soluble hydric chloride is than chlorine.

91. The solution of the gas obtained as above is the body known as hydrochloric acid, though it is really only a watery solution containing at the most about 40 per cent. of hydric chloride. When this body is manufactured on a large scale for commercial purposes, iron vessels are employed, and no particular care is taken to prevent impurities of various kinds getting into the product, which has consequently a yellow colour, and is of no

use in the laboratory except for making chlorine, carbonic acid, &c. It is sold under the names of muriatic acid and spirits of salt.

Water at the freezing point is capable of dissolving about 550 times its volume of hydric chloride, becoming thereby much denser, *i. e.*, heavier, bulk for bulk, than pure water. Water

Fig. 38.

at high temperatures dissolves less of the gas, therefore if we take a solution of it which has been saturated at a low temperature and boil it, a considerable part of the hydric chloride will be given off, and that too so abundantly and readily, that it forms a very convenient way of obtaining a small quantity of the gas for any purpose (fig. 38).* It may here again be remarked that *all* gases are less soluble in hot than in cold water. From these experiments and accompanying observations we learn that hydric chloride is a gas, which is heavier than air, colourless, and transparent; acid in reaction, but devoid of bleaching powers; very soluble in water, and incapable of burning or supporting combustion.

92. The quantitative demonstration of its composition by volume is too difficult for any but a practised chemist to attempt, except in a somewhat rough manner. The following experiment succeeds very well if conducted carefully.

* The yellow commercial acid, if of good quality, *i.e.* strong, may be used.

Provide a graduated tube with a well fitting and slightly greased india-rubber plug; fill it *completely* with dry hydric chloride gas by displacement, or better over mercury; introduce a small thin sealed glass bulb of the size shown full of zinc filings, close the mouth of the graduated tube with its stopper; shake it violently, so as to break the little bulb, and spread its contents over the inside. Set by for ten minutes or so. A rapid action ensues.

Fig. 39.

$$Zn + 2\,H\,Cl = Zn\,Cl_2 + H_2,$$

that is, the zinc takes the chlorine from the hydrogen and leaves the latter free. Open the mouth of the tube well below the surface of water, this will rush up and fill *exactly half* the space: this proves that a volume of hydric chloride contains half its volume of hydrogen.

93. If a mixture of exactly equal volumes of chlorine and hydrogen be made, and then caused to explode by exposure to the light of the sun, or that of the electric lamp, a volume of hydric chloride exactly equal to that of the mixture will be produced, which may be represented thus:

Cl = 35·5	+	H = 1	=	$\frac{HCl}{2} = 18{\cdot}25$	$\frac{H\,Cl}{2} = 18{\cdot}25$

which proves that hydric chloride contains half its volume of hydrogen and half of chlorine united without condensation.

94. The composition of hydric chloride by weight might be determined in a manner similar to that used in the determination of the composition of water by weight (see § 53), only substituting some easily reduced chloride, such as argentic chloride, for the cupric oxide, and replacing the last chloride of calcium tube by one containing solid caustic potash (potassic hydrate). The reaction of the hydrogen on the silver chloride is represented by—

$$2\,(Ag\,Cl) + H_2 = Ag_2 + 2\,H\,Cl.$$

Now, if the silver chloride and its tube be weighed before and

after the experiment, and also the terminal potash tubes, it is evident, that what the first loses is the chlorine, and what the latter gains is the hydric chloride formed by the reaction; the difference must therefore be the hydrogen. Hydrogen being taken as unity and the numbers being reduced to their simplest expression, we shall find that for every one part of hydrogen we shall have 35·5 parts of chlorine.

This experiment also serves to determine the atomic weight of chlorine, for it shows that the quantity of that body which combines with the unit weight of hydrogen is 35·5 times heavier than the hydrogen; and as it has been shown before, that in hydric chloride there are *equal* volumes of the two constituents, it follows from what has been said in § 58, that there are an equal number of atoms of each, and that therefore the atomic weight of chlorine is 35·5 times that of hydrogen.

95. The more purely chemical of the properties of hydric chloride may be examined in the following order. The method of demonstrating each will readily occur to the operator where specific directions are not given. Note, the solution of the gas may be employed.

Firstly, its action on metals. Potassium and sodium dissolve with great violence and evolution of hydrogen, *e. g.*,

$$K_2 + 2\ H\,Cl = H_2 + 2\ K\,Cl.$$

If you try this, throw a very small bit of the metal on the surface of some of the acid liquid, and get out of the way.

Magnesium, zinc, iron, and aluminium dissolve with ease, evolving hydrogen, and forming $Mg\,Cl_2$, $Zn\,Cl_2$, $Fe\,Cl_2$ and Al_2Cl_6; the equation in the last case being $Al_2 + 6\,HCl = 3\,H_2 + Al_2\,Cl_6$.

Tin dissolves with rather more difficulty, requiring heat to accelerate the action, and forming stannous chloride, $Sn\,Cl_2$.

Copper dissolves very slowly, even at the boiling temperature, to form $Cu_2\,Cl_2$.

Lead and silver are superficially converted into chlorides, the

action extending further in the case of lead than in that of silver, perhaps because of the more porous nature of lead chloride.

Mercury, gold, and platinum are unaffected even by prolonged boiling in the acid liquid; and bismuth, antimony, and arsenic are barely attacked by it.

96**. Secondly, its action on metallic oxides. All basic metallic oxides are acted on by hydric chloride with production of a metallic chloride and water, *e.g.*,

$$Ag_2O + 2HCl = 2AgCl + H_2O,$$
$$CuO + 2HCl = CuCl_2 + H_2O,$$
$$Bi_2O_3 + 6HCl = 2BiCl_3 + 3H_2O.$$

If the resulting metallic chloride is decomposed by heat, then more or less chlorine will be given off at the same time, *e.g.*,

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O; \text{ but } MnCl_4 = MnCl_2 + Cl_2,$$
$$2CrO_3 + 12HCl = Cr_2Cl_6 + 6H_2O + 3Cl_2.$$

The chlorides of those metals which are not readily soluble in solution of hydric chloride, and of those which are difficult to obtain, are prepared in this manner, with the exception of those of gold and platinum, for which see "Aqua Regia," § 98.

97**. Thirdly, the actions it exerts on metallic salts are not to be reduced to a general statement, but must be considered separately. (1°) Where the metal present forms a soluble chloride, and the corresponding hydrogen salt is either much more volatile than hydric chloride, or is insoluble in that body. In this case, chlorine combines with the metal, and the hydrogen salt (or the products of its decomposition) formed, either goes off as gas or vapour, or is precipitated, *e.g.*,

$$\underbrace{CaCO_3}_{\text{Calcic carbonate.}} + 2HCl = CaCl_2 + H_2O + \underbrace{CO_2}_{\text{Carbonic acid gas.}}, \text{ which goes off}$$

$$\underbrace{Na_4SiO_4}_{\text{Sodic ortho-silicate.}} + 4HCl = 4NaCl + \underbrace{H_4SiO_4}_{\text{Hydric ortho-silicate.}}, \text{ which precipitates.}$$

In these cases the action is determined by the hydrogen salt formed from the metallic salt being removed from the sphere of action and so prevented from effecting the reverse action, which would be represented by reading

the above equation backwards. (2°) Where the metal present forms a compound with chlorine *less* soluble than the original salt, *e.g.*,

$$\underbrace{AgNO_3}_{\text{Silver nitrate.}} + HCl = \underbrace{AgCl}_{\text{Silver chloride.}} + \underbrace{HNO_3}_{\text{Hydric nitrate.}}.$$

Silver chloride being insoluble separates in the solid form from the solution, and hydric nitrate (hydrated nitric acid) remains in solution, and

$$\underbrace{Pb(NO_3)_2}_{\text{Lead nitrate.}} + 2HCl = PbCl_2 + 2HNO_3.$$

Lead chloride being only slightly soluble is thrown down.

$$\underbrace{Hg_2(NO_3)_2}_{\text{Mercurous nitrate.}} + 2HCl = \underbrace{Hg_2Cl_2}_{\text{Mercurous chloride.}} + 2HNO_3.$$

Mercurous chloride being insoluble is precipitated.

98. Besides the methods already given of preparing metallic chlorides, there is yet one other important one, which consists in dissolving the metal, its oxide, sulphide, &c., in a mixture of hydric nitrate and hydric chloride, called "aqua regia." This last method is more especially made use of in preparing the chlorides of those metals which are insoluble in hydric chloride, and of which it is difficult to obtain the oxides. Such are gold and platinum, which do not dissolve in the least in hydric chloride, but do so with tolerable ease in a mixture of that body with hydric nitrate, HNO_3. Aqua regia is a liquid in which chlorine is being perpetually set free by the oxidation of the hydrogen of the hydric chloride, at the expense of the oxygen of the hydric nitrate. This chlorine at the moment of its liberation is said to be "nascent," and is then endowed with even more powerful combining properties than when free; probably because it is not yet united to another atom of chlorine to constitute a molecule (see § 62). It accordingly unites with the metal present to form a chloride.

99. The solution of any chloride being made, it may be desired to obtain the salt in a solid form, an object which may

be attained in many cases by evaporating off the water present at a gentle heat, until crystals begin to appear in or on the liquid, and then allowing the whole to cool. Now as most salts are more soluble in hot than in cold water, it follows that the solution concentrated as directed, and so *saturated*, at a high temperature, will, on being allowed to cool, deposit some of the salt in a solid form, only so much remaining in solution as the water present can dissolve when cold. The salt is of course deposited slowly, and consequently the particles of it have time to arrange themselves in any way that their attractive forces on one another may direct. It is found, accordingly, that very few soluble salts separate from their aqueous solutions in amorphous masses; nearly all take forms more or less regular, the bounding surfaces being flat, and the edges formed by the meeting of two faces consequently straight. These regularly formed masses, whether transparent or not, are called crystals.

100. Sometimes the crystals are composed only of the salt proper, as in the case of mercuric chloride, $HgCl_2$, and sodic chloride, NaCl; but more often they contain in addition water, held in some loose and little understood manner, and called water of crystallisation, as for example: Crystallised chloride of barium contains two molecules of water in addition to the salt $BaCl_2$, and therefore has the composition $BaCl_2, 2H_2O$; likewise ferrous chloride, $FeCl_2$, crystallises with four molecules of water, producing $FeCl_2, 4H_2O$, and so with most salts besides the chlorides. This water of crystallisation can usually be driven off by the application of heat, or even in some cases by exposing the crystals to a dry atmosphere.

101. The presence of a soluble chloride in any acid liquid is very readily detected by adding to the suspected liquid some solution of silver nitrate, when the silver chloride is formed as a white precipitate which clots together when shaken, turns purplish on exposure to daylight, is insoluble in hot hydric nitrate, but readily soluble in ammonia; and which, when collected, dried, and fused in a porcelain crucible over a lamp, does not undergo any decomposition.

Mercurous nitrate, $Hg_2(NO_3)_2$, gives in solutions of chlorides a white precipitate of Hg_2Cl_2 (calomel), mercurous chloride, which when washed turns black on addition of ammonia.

Lead nitrate $Pb(NO_3)_2$ or lead acetate $Pb(C_2H_3O_2)_2$ solution give in moderately strong solutions of a chloride, a white crystalline precipitate of $PbCl_2$, which dissolves when boiled with much water, and crystallises out again on cooling in beautiful little shining needle-shaped crystals.

When a chloride is heated in a test tube with binoxide of manganese and hydric sulphate, chlorine is evolved, and can be recognised even when in small quantity by its smell, and by its power of bleaching a bit of moist litmus paper held over the mouth of the tube.

These reactions are quite characteristic when taken all together.

102. The quantity of chlorine present in the form of a chloride in any given solution, can be estimated by precipitating it all as silver chloride—by the addition of an *excess* of silver nitrate to the solution previously rendered acid by hydric nitrate; collecting the precipitate on a filter, washing, drying, and igniting it and the filter till the latter is burnt to a white ash, in a weighed porcelain crucible; deducting the weight of the crucible and the weight of the ash of a similar filter, the weight of silver chloride is obtained. From this weight the weight of the chlorine present in the original substance is easily calculated. Suppose we have obtained ·75 grammes of silver chloride, then since Ag = 108, and Cl = 35·5, Ag Cl = 143·5, of which 35·5 are chlorine,

$\therefore$ every gramme of silver chloride contains $\frac{35{\cdot}5}{143{\cdot}5}$ grammes of chlorine, and ·75 grammes $\therefore$ contains $\frac{35{\cdot}5}{143{\cdot}5} \times \frac{{\cdot}75}{1} = {\cdot}1855$ grammes chlorine in the original substance.

COMPOUNDS OF CHLORINE WITH OXYGEN.

103. Chlorine does not unite directly with oxygen, nevertheless many compounds of them can be obtained by indirect means.

The following are either already known, or will doubtlessly soon be discovered. Those not yet prepared are marked by an asterisk :—

Cl_2O,	Chlorous oxide, or	Chloric protoxide, also hypochlorous acid.
*Cl_2O_2,	Chloric oxide, or	Chloric dioxide.
Cl_2O_3,	Chlorous acid (anhydrous) or . .	Chloric trioxide.
Cl_2O_4,	Chloric peroxide, or	Chloric tetroxide.
*Cl_2O_5,	Chloric acid (anhydrous) or . .	Chloric pentoxide.
*Cl_2O_6,		Chloric hexoxide.
*Cl_2O_7,	Perchloric acid (anhydrous) or . .	Chloric heptoxide.

Observe carefully the terminations of the names—

Cl_2O, Chlor*ous* oxide.	Cl_2O_2, Chlor*ic* oxide.
Cl_2O_3, Chlor*ous* acid.	Cl_2O_5, Chlor*ic* acid.

The first two, both called oxides, are distinguished by giving the termination *ous* to the one containing least oxygen, and *ic* to the other; and so with the other pair. The prefix *hypo* means "below," and is used to distinguish Cl_2O from Cl_2O_3 when it is called an acid. *Hypo*chlorous acid therefore means an acid below (in oxidation) chlor*ous* acid, which again is below chlor*ic* acid, Cl_2O_5. *Per*, a contraction of hyper, means above; therefore *per*chloric acid is an acid above chloric in its degree of oxidation.

104. Cl_2O can be made by passing dry chlorine gas over mercuric oxide kept cold,

$$HgO + 2\,Cl_2 = HgCl_2 + Cl_2O,$$

and condensing the yellowish gas so obtained by leading it into a small flask surrounded with ice and salt. It is of no use, it will not keep, but is very apt to explode violently even when standing by itself in a cold place. Its chief interest lies in its reaction with water; when brought into contact with that body it exchanges one atom of its chlorine for an equivalent of hydro-

gen, while the chlorine which it gives up takes the place of the hydrogen so abstracted from the water,

Chloric protoxide.

$$\begin{matrix}\text{hydric} \\ \text{hypochlorite}\end{matrix}\left\{\begin{matrix}\overbrace{\text{Cl O}} \\ \text{H}\end{matrix}\middle|\begin{matrix}\overbrace{\text{Cl}} \\ \text{O H}\end{matrix}\right\}\begin{matrix}\text{hydric} \\ \text{hypochlorite.}\end{matrix}$$

water.

Or in the form of an equation—

$$\overbrace{\text{Cl}_2\text{O}}^{\text{Chlorous oxide.}} + \text{H}_2\text{O} = \overbrace{2\ \text{H Cl O.}}^{\text{Hydric hypochlorite.}}$$

Conversely, if we abstract the elements of water from two molecules of hydric hypochlorite, we get chlorous oxide—

$$2\ \text{Cl HO} - \text{H}_2\text{O} = \text{Cl}_2\text{O.}$$

Hydric hypochlor*ite*, H Cl O, has the composition of an oxide of hydric chloride, and can indeed be made by the direct addition of oxygen (in the nascent state) to that body. Observe the termination *ite*, as all bodies which form hydrogen salts and the names of which end in *ous*, give derivatives ending in *ite*. The hydrogen of hydric hypochlorite may be replaced by *equivalent* quantities of metals to form metallic hypochlorites, such as K Cl O, Zn $(\text{Cl O})_2$, &c., by acting on it with the corresponding hydrate or oxide, *e.g.*,

$$\text{K HO} + \text{H Cl O} = \text{K Cl O} + \text{H}_2\text{O or}\begin{matrix}\text{K} \\ \text{Cl O}\end{matrix}\middle|\begin{matrix}\text{H O} \\ \text{H}\end{matrix}$$

$$\text{Zn O} + 2\ \text{H Cl O} = \text{Zn}(\text{Cl O})_2 + \text{H}_2\text{O or}\begin{matrix}\text{Cl O} \\ \text{Cl O} \\ \text{Zn}\end{matrix}\middle|\begin{matrix}\text{H} \\ \text{H} \\ \text{O}\end{matrix}$$

but not by using the metals themselves, because the nascent hydrogen reduces the hypochlorite, and so only a metallic chloride is obtained.

105. The hypochlorites of potassium and sodium are important, as they constitute the active part of the bleaching and disinfecting solutions of commerce.

When chlorine is passed into a *cold* solution of potash (K HO)

$$\text{we get} \quad 2\,K\,HO + Cl_2 = K\,Cl + K\,Cl\,O + H_2\,O,$$

that is, a mixture of the chloride and the hypochlorite, of the metal.

Hydric hypochlorite, and metallic hypochlorites give up their oxygen with the utmost readiness to many bodies of organic origin, especially to colouring matters and the foul products of putrefaction. This addition of oxygen destroys the bodies, burns them in fact, and therefore destroys the colour in the one case and the smell in the other.

To demonstrate the truth of the latter statements, take about an ounce of fresh chlorine water,* or the newly prepared and filtered solution of bleaching powder (commercially called chloride of lime), add to it solution of silver nitrate until nothing more is precipitated, and filter. In this way you will remove all the chlorine which is present as a chloride, but leave in solution that which exists as a hypochlorite, because argentic hypochlorite is soluble. Of course, excess of silver nitrate will remain in the liquid. Divide the clear solution into two parts, acidulate one with hydric sulphate, and add some solution of sulphate of indigo, which will be immediately bleached, and a fresh precipitate of silver chloride formed by the *reduction* of the hypochlorite—

$$Ag\,Cl\,O - O = Ag\,Cl.$$

To the other portion add, say a portion of some game bird which is "high," the smell of putrefaction will be destroyed. The process of bleaching, as carried out on a large scale, may be illustrated thus: Prepare a weak solution of bleaching powder (commercial chloride of lime); then stamp a piece of red cotton cloth in various places with a mixture of tartaric acid and gum; when this is partially dry pass the cloth through the solution of bleaching powder, and you will find that those parts of the cloth which were rendered acid become bleached, while the remainder is unaltered. From this, one learns that metallic hypochlorites do not decompose and part with their oxygen so readily as hydric hypochlorite; because, the action of the tartaric acid is to take away the calcium of the calcic

* Which may be regarded as a mixture of hydric chloride and hypochlorite produced by the re-action

$$Cl_2 + H_2O = HCl + HClO.$$

hypochlorite, and replace it by hydrogen at those spots where the mixture was placed.*

Chloric dioxide is unknown, and chloric trioxide uninteresting.

106. Chloric peroxide, $Cl_2 O_4$, is a gas which is made by the action of hydric sulphate on potassic chlorate; it is yellowish green, and decomposes with a most violent explosion at a temperature little above that of the air.

Note. Be careful not to heat potassic chlorate with oil of vitriol.

107. Chloric pentoxide, $Cl_2 O_5$, or anhydrous chloric acid, is unknown, but the body which it would form by acting on water is $H Cl O_3$, hydric chlorate, a well-known and interesting substance,

$$Cl_2 O_5 + H_2 O = 2 H Cl O_3,$$

especially in its metallic derivative, $K Cl O_3$, potassic chlorate. Observe that anhydrous chlor*ic* acid gives $H Cl O_3$ and $K Cl O_3$, hydric and potassic chlor*ate*; and further, that all acids the names of which end in *ic*, give salts the names of which terminate in *ate*.

108. Potassic chlorate is made thus: Pass chlorine to saturation (*i.e.*, till no more is absorbed) into a strong solution of three or four ounces of potash (KHO); this will make a mixture of potassic chloride and potassic hypochlorite; then boil the solution for some time. The atoms of the hypochlorite will re-arrange themselves in a way which may be represented,

$$3 K Cl O = K Cl O_3 + 2 K Cl;$$

that is, two molecules of the salt will give up their oxygen to a third molecule to form the chlorate. As it takes two atoms of chlorine to form one molecule of potassic hypochlorite, and three of this last to give one of chlorate, it takes six of chlorine altogether to make a molecule of chlorate,

$$3 Cl_2 + 6 K H O = K Cl O_3 + 5 K Cl + 3 H_2 O.$$

The mixture of chloride and chlorate obtained by this process is a very good one on which to practise the separation of two bodies by crystallisation, for the latter is much less soluble in water than the former.

* This experiment often fails in the hands of those who try it for the first time.

109. Evaporate the boiled and filtered solution of the two salts till a crust begins to form on the surface of the liquid; then set the whole aside for a night. The chlorate will crytallise out, together with a small quantity of chloride; while the solution will contain most of the latter, and just such a portion of the former as can be retained by the water present, when cold. Pour away this mother liquor, and drain the crystals on a pad of blotting-paper, or a dry porous tile, in order to remove from them as great a quantity of the solution of potassic chloride as possible. Then dissolve the salt in the least possible quantity of boiling distilled water, and again set aside. The new crop of crystals so obtained, will obviously be much purer than the first; for as they were only mixed with a small quantity of chloride, and as that body is very soluble, it will now remain entirely in solution, while the crystals will be pure. Though pure in themselves, yet they will remain wet with the still impure mother liquid, however carefully they are drained, and if then dried will retain some of the chloride. Therefore, the process of crystallisation and draining must be repeated till a small portion when dissolved in water gives no cloudiness with a solution of silver nitrate. This of course implies that silver chlo*rate* is not insoluble, though silver chlo*ride* is.

Potassic chlorate crystallises in fine transparent tables, which have the composition $K Cl O_3$.

110. Hydric chlorate, $H Cl O_3$, otherwise called hydrated chloric acid, can be prepared from potassic chlorate by replacing the potassium of the latter by hydrogen. This is effected by means of hydric fluosilicate, $H_2 Si F_6$,*

$$2 K Cl O_3 + H_2 Si F_6 = K_2 Si F_6 + 2 H Cl O_3.$$

The potassic fluosilicate being insoluble is precipitated, and can be removed by filtration through a plug of gun cotton or asbestos; and the aqueous solution of hydric chlorate concentrated by keeping it in an air-pump vacuum over the surface of the oil of vitriol, which absorbs the vapour of the water as fast as it is formed.

It is a somewhat oily liquid, which decomposes rapidly at a boiling heat. When concentrated, it oxidises organic bodies so rapidly that it sometimes sets fire to them.

111. From hydric chlorate any required metallic chlorate may

* For the reason of not using hydric sulphate, see § 106.

be prepared, by neutralising it with the oxide or carbonate of the metal, *e.g.*,

$$Ba\,O + 2\,H\,Cl\,O_3 = Ba\,(Cl\,O_3)_2 + H_2\,O$$
$$Pb\,O + 2\,H\,Cl\,O_3 = Pb\,(Cl\,O_3)_2 + H_2\,O.$$

All metallic chlorates are soluble in water, they are all decomposed by heat, giving up all or part of their oxygen, and leaving the metal either as oxide or chloride. All chlorates part with oxygen readily to other bodies which combine with it, especially when heated, and for this reason they are much used in the manufacture of fire-works.

Powder some potassic chlorate very fine, and mix it with about its own weight of sugar (which contains oxygen, hydrogen, and carbon), which has been *separately* powdered; set light to the mixture. The oxygen of the chlorate will combine with the carbon and hydrogen of the sugar with so much energy that the whole mass will burn with a fierce flame of a violet tint. Baric chlorate, similarly treated, gives a bright green fire.

Other chlorates give, under similar circumstances, "fires" of hues varying with the metal present. So easily does potassic chlorate part with its oxygen to some bodies, like sulphur, that it is only necessary to rub it with them in order to cause combustion, which is generally so rapid as to amount to an explosion. To try this, operate on small quantities only for fear of accident; a single grain of the chlorate rubbed with an equal quantity of sulphur in a mortar will give a series of sharp detonations; or if the two bodies be mixed together on paper with a slip of card, wrapped up, and struck smartly with a hammer, a loud explosion will be produced. Gun caps were at one time charged with such a mixture. The heads of lucifer matches consist of a mixture of potassic chlorate, phosphorus, gum, &c.

112. As all chlorates are soluble, their presence in a solution cannot be recognised by causing them to form a precipitate; but as they are readily reduced to chlorides, it is only necessary first to remove from the liquid under examination any chlorine in the form of chlorides that may be present by addition of excess of silver nitrate, to filter off the precipitate, and then to

reduce the chlorates present (if any), by acidulating the liquid with hydric sulphate and adding a strip of zinc. The hydrogen, as it is liberated from combination (*i.e.*, while in the nascent state), robs the chlorate of its oxygen and reduces it to a chloride, the presence of which is immediately recognised by further addition of silver nitrate causing a precipitation of silver chloride. Also a solution of a chlorate when heated with hydric sulphate, gives rise to the characteristic smell of chloric tetroxide.

113. If potassic chlorate be kept fused till a considerable quantity of oxygen has been expelled from it, then cooled, and the mass submitted to crystallisation, a very slightly soluble salt, having the composition $K Cl O_4$, will separate out,

$$2 K Cl O_3 = K Cl + O_2 + K Cl O_4.$$

Potassic perchlorate, though containing more oxygen than potassic chlorate, parts with that element much less readily; indeed, perchlorates generally are more stable than the corresponding chlorates. For instance, if potassic perchlorate be distilled with hydric sulphate, hydric perchlorate is produced.

$$K Cl O_4 + H_2 S O_4 = H Cl O_4 + H K S O_4.$$

(Compare § 106.) This is a fuming, colourless liquid, which is so powerful an oxidising agent, that if only thrown on paper it sets it on fire.

Note.—If you prepare either hydric chlorate or perchlorate be careful not to get them about your hands, as either will produce wounds which are very difficult to heal.

If we could deprive hydric perchlorate of water we should obtain $Cl_2 O_7$,

$$2 H Cl O_4 - H_2 O = Cl_2 O_7.$$

114. Observe, from the foregoing experiments and observations, that chlorine unites with the greatest readiness with hydrogen to form a compound which is exceedingly stable; but that the oxygen compounds of it are easily decomposed.

QUESTIONS ON CHAPTER VI.

1. (*a*) Describe the preparation of chlorine; (*b*) enumerate its properties.

2. (*a*) What gas is set free when HCl is heated with MnO_2? (*b*) Give the reaction in symbols. (*c*) Describe the gas and its properties.

3. Describe the effects produced by chlorine on the following substances:—indigo solution, copper foil, powdered antimony, powdered charcoal, a lighted candle, and dry litmus paper.

4. What weight of pure binoxide of manganese must be heated with hydric chloride to give 71 grammes of chlorine (Mn = 55)?—*Ans.* 87 grms.

5. What volume would the 71 grammes of chlorine occupy?—*Ans.* 22·4 litres.

6. What weight of pure manganic dioxide must be used to prepare 3 litres of chlorine?—*Ans.* 11·65 grammes.

7. What volume of chlorine would be required to transform a cubic inch of hydrogen into hydric chloride?—*Ans.* 1 cubic inch.

8. Give the formulæ of the chlorides of the elements represented by K′, Na′, Ba″, Ca″, Zn″, Pb″, Ag′, Bi‴, As‴, and name each.

9. By what reaction can the sodium of sodic chloride (common salt) be replaced by hydrogen? Give an equation of the reaction.

10. What weight of sodic chloride must be used to prepare 100 grammes of hydric chloride?—*Ans.* 160·27 grammes.

11. What weight of hydric chloride would be given by the use of 100 grammes of sodic chloride?—*Ans.* 62·39 grammes.

12. What is the specific gravity of hydric chloride as compared with air (calculated)?—*Ans.* 1·267.

13. Describe the physical properties of *hydrochloric acid gas.*

14. Why does it "fume" when it comes into contact with moist air?

15. How could you demonstrate the composition of hydric chloride by volume? What is that composition?

16. If 78·5 cubic centimetres of hydric chloride could be completely decomposed, what volume of chlorine and what of hydrogen would be obtained?—*Ans.* 39·25 cubic centimetres of each.

17. How could the composition, of hydric chloride, by weight be determined?

18. If 5 grammes of silver chloride were completely decomposed by heating in hydrogen, what weight of hydric chloride would be made?—*Ans.* 1·271 grammes.

19. In 100 parts by weight of chloride of silver, how many parts silver (Ag = 108)?—*Ans.* 75·261 parts.

20. What metals dissolve readily in solution of hydric chloride? What is the action of hydric chloride on metallic oxides?

21. Explain the action of "aqua regia" in converting gold into its chloride.

22. What is a crystal? Under what conditions may crystals be obtained from a liquid? What is water of crystallisation?

23. How can the presence of a chloride in a solution be detected (give *all* the tests)?

24. How may the quantity of chlorine present in a solution (in the form of a chloride) be estimated?

25. How many grains of silver nitrate are required to precipitate all the chlorine in 10 grains of sodium chloride?—*Ans.* 29·06 grammes, nearly.

26. Give a list of the possible oxides of chlorine, with their names and symbols.

27. What takes place when chlorine is passed into a cold solution of potash (KHO)?

28. What are hypochlorites used for? How is it they bleach?

29. Why does wet chlorine bleach, but not dry?

30. (*a*) What gas is produced when hydric sulphate acts on potassic chlorate? (*b*) What property renders its preparation dangerous?

31. How is pure potassic chlorate prepared?

32. How much chlorine must I use to make one ounce of potassic chlorate?—*Ans.* 1·738 ounces.

33. What are the chlorates used for? Why are they applicable for this purpose?

34. How can the presence of a chlorate in solution be detected?

35. What are the conditions necessary in order that chlorine may bleach? To what is the bleaching action due?

36. How is it that "aqua regia" has a more powerful action on gold, platinum, &c., than free chlorine has?

37. If 50 cubic centimetres of hydrogen will diffuse into an atmosphere of chlorine through a given aperture in 5 minutes, how much chlorine will diffuse into the hydrogen in the same time (both gases being supposed to have unlimited volume and to remain at the same pressure)?

$\sqrt{1}=1$ $\qquad$ $\sqrt{35{\cdot}5}=5{\cdot}9582$

$\therefore$ hydrogen which diffuses $=\frac{50}{1}$ and chlorine $=\frac{50}{5{\cdot}9582}$.

CHAPTER VII.

BROMINE, IODINE, AND FLUORINE.

BROMINE.—Symbol Br, Atomic weight 80.

Combining vol. 1, or $\left.\begin{array}{|c|}\hline 80 \\ \hline \end{array}\ \begin{matrix}\mathrm{Br}\\ \mathrm{Br}\end{matrix}\right\} = 2$ vols. 160.

115. THIS element much resembles chlorine in its properties, but also differs from it in several important particulars. It is obtained from sea-water. Bromine is a liquid of a dark brown red colour at ordinary temperatures, but when heated to 45° C., boils (*i. e.*, gives off bubbles of vapour), and is converted into a dark red gas, which again condenses into the liquid form when cooled. If liquid bromine is cooled to —22° C. it solidifies into a metallic-looking solid. Bromine, like chlorine, combines directly with hydrogen, but with far more difficulty, to form a hydride (H Br), which is more easily decomposed into its constituents than hydric chloride is. Bromine also forms metallic bromides, analogous to the corresponding chlorides, both in composition and properties, but which are, generally speaking, less soluble and less stable.

With oxygen, on the other hand, it combines more freely to form compounds which are not so inclined to split up into their constituents. Bromine bleaches, but not so strongly as chlorine. A metallic bromide is decomposed by chlorine, which turns the bromine out of combination and takes its place, thus,—

$$2\ \mathrm{K\ Br} + \mathrm{Cl_2} = 2\ \mathrm{K\ Cl} + \mathrm{Br_2}.$$

As bromine occurs rarely, and even then only in small quantities, it is not sufficiently important to claim close study from a beginner.

IODINE.—Symbol I, Atomic weight 127.

Combining vol. 1, or $\left.\begin{matrix}\boxed{127}\\ \end{matrix}\right\} \begin{matrix}\text{I}\\ \text{I}\end{matrix}\Big\} = 2$ vols. = 254.

116. This element, the third one of our group of monovalent elements, has analogies both to chlorine and bromine, but differs more from the first than from the second.

Iodine, like chlorine, never occurs free in nature, but is always found combined with metals, chiefly sodium and magnesium, in the water of the sea, and of some mineral springs. Its principal source is "kelp," which is the ash of certain ocean sea weeds. The kelp is digested with water which dissolves out many salts, *e. g.*, carbonate of soda, chlorides of sodium and potassium, iodides of sodium and magnesium, &c., &c. This mixture of salts is evaporated, and the less soluble ones raked out as they are deposited, until a mother liquid very rich in iodides is obtained; this is then mixed with manganic dioxide and oil of vitriol, and the whole distilled at a gentle heat in a leaden retort, and the evolved vapours of iodine condensed in a series of glass globes. The reaction which takes place is similar to that described in the case of chlorine in § 72.

$$2\,NaI + MnO_2 + 3\,H_2SO_4 = 2\,NaHSO_4 + MnSO_4 + 2\,H_2O + I_2$$

This operation may be performed on a small scale, by introducing about a quarter of an ounce of potassic iodide, K I, into a retort, together with an equal weight of black oxide of manganese, adding some slightly diluted hydric sulphate, and distilling slowly.

In carrying this out it will be observed that the vapour of iodine which rises is of a beautiful violet hue, and that when that vapour reaches the cool part of the neck of the retort it condenses into shining black scales, which have all the look of a metal.

117. Place a few fragments of iodine at the bottom of a Florence oil-flask and apply heat. The iodine will first melt into a dark liquid, and then give off the before-mentioned violet gas, which is obviously much

heavier than air, and which again condenses on the upper and colder parts of the flask into solid iodine.

Notice here that these three elements,—chlorine, bromine, and iodine, show that the three states of matter, viz., solid, liquid, and gaseous, depend not on essential differences of constitution, but on differences in the temperature required to bring them all to the same form; thus, chlorine strongly cooled becomes a liquid, which is the form bromine has at ordinary temperatures, while iodine must be heated to 107° C. before it assumes the same state. Or, again, chlorine is a gas even at 0° C.; bromine does not become aëriform till 45° C. is reached, and iodine not till 180° C.

118. If solid iodine is introduced into a narrow-necked flask of known capacity, the weight of which when *empty* is known, and if then the flask is plunged into a bath of oil maintained at a temperature considerably higher than the boiling point of iodine, say 200° C., the iodine is converted into vapour, which drives the air out of the flask and then continues to issue forth itself till no more liquid iodine remains to be boiled away. When the last portion of iodine has assumed the gaseous form, the flask will be *full* of vapour of iodine at a temperature of 200° C.; if now the mouth of the flask is sealed by the blow-pipe flame while the temperature is still maintained, there is obtained a known volume of the vapour of iodine at 200° C. Suppose the flask removed from the bath, cleaned, and weighed when cold, the weight found will be that of the glass flask plus that of the iodine contained. If from this weight that of the flask alone be subtracted, the weight of iodine will be obtained, knowing by calculation what weight of air or of hydrogen would be contained by the flask at 200° C., this experiment gives the means of determining the *Vapour Density* of iodine.

Suppose the air-free flask weighed . . . 45·5 grammes,
the capacity of it was . . . . . 300 cu. cent.
its weight, when containing the iodine, which was sufficient to fill it with pure vapour at 200° C. . . . = 47·4634 grms.

The weight of iodine must . . . = 1·9634;
but the weight of 300 cubic centimetres of hydrogen at 200° C. is 0·01546 grammes,* and $\frac{1·9634}{0·01546} = 127$ nearly.

So the experiment shows that the vapour of iodine is 127 times as heavy as hydrogen at the same temperature.

As all gases expand and contract at the same rate, for equal variations of temperature, this proportion must hold good for all temperatures, and so we are justified in saying that if it was possible to weigh 11·2 litres of iodine vapour at 0° C., and 760 millimetres, barometric pressure, they would be found to be 127 grammes in weight.

The vapour density of water, and other volatile liquids and solids, is determined in a like manner.

119. Iodine is but very slightly soluble in water, as may be shown by shaking some in a powdered form with that liquid, which will thereby acquire only a pale brown colour.

Its specific gravity in the solid form is 4·95.

Iodine does not unite readily with hydrogen.

120. Expose a few grains of iodine in a bottle of hydrogen to the direct rays of the sun. Even after the lapse of many hours, the two will not have united in the slightest degree, as will be shown by there having been no production of acid vapours (tried by litmus paper introduced into the bottle). Iodine vapour passed, together with hydrogen, through a red-hot tube, unites partially, forming hydric iodide, H I.

121. Though iodine unites with such difficulty with hydrogen, it almost rivals chlorine in its power of combining with metals.

Rub together, in a warm mortar, mercury and iodine in the proportion of two *atoms* iodine to one of mercury (perform the operation in a draught). The two unite slowly at first, and then more and more rapidly as the temperature rises from the heat evolved by the combination of the first portions, until at last the remaining portions of the uncombined elements

* $\frac{273}{273+200}$ of $\frac{300}{11,200}$ of 1 = 0·01546.

unite in a sudden and almost violent manner. The product, which has a fine vermilion colour, is mercuric iodide HgI_2.

Zinc warmed with iodine in presence of water unites with it, and forms zinc iodide ZnI_2, which remains dissolved in the liquid. In performing this experiment it will be noticed after a few minutes the liquid becomes coloured dark brownish-red, and then at last gets colourless again. Iodine, though very little soluble in water, dissolves easily in solutions of metallic iodides.

By help of this last statement explain the foregoing.

Iodine does not bleach, probably because it forms no hydric hypoiodite (HIO), (see § 105). The atomic weight of iodine is 127, and therefore, its vapour density as compared to hydrogen is 127, and as compared to air $\frac{127}{14{\cdot}4}$.

The presence of *free* iodine in any liquid is readily detected by taking advantage of its power to form a deep blue compound with starch paste. To show this property of it, dissolve a grain or two of iodine in a weak solution of iodide of potassium, and add a little of the liquid so prepared to starch water (prepared by putting a small quantity of starch into boiling water, and then allowing it to cool).

Hydric Iodide or Hydriodic Acid.

$$HI = 1 + 127 = 128 = \boxed{64}\,\boxed{64}$$

122. As iodine unites with hydrogen in a very imperfect manner, even under the influence of a high temperature, hydric iodide must be prepared by some indirect means. The first plan which will occur to the mind of the student is one analogous to that followed in the actual preparation of hydric chloride, *i. e.*, the distillation of a metallic iodide with oil of vitriol.

$$KI + H_2SO_4 = HI + HKSO_4$$

is an equation so like

$$NaCl + H_2SO_4 = HCl + HNaSO_4,$$

that taking into consideration the similarity of iodine and chlorine, one is almost justified in anticipating the success of the method. But though the reaction does occur as the equation indicates, hydric iodide cannot be so prepared, for the bond of union between the two elements is so slight, that the greater part of the first formed hydric iodide gives up its hydrogen to some of the oxygen of the oil of vitriol employed, and, therefore, iodine is set free.

Put a few crystals of potassic iodide into a test-tube, and pour over them a little hydric sulphate and apply heat. Violet vapours of iodine will be given off together with a few white fumes of undecomposed hydric iodide, and at the same time a smell of burning sulphur will be perceptible, owing to the production of sulphuric dioxide, SO_2. The hydric iodide acts on the hydric sulphate thus,

$$2HI + H_2SO_4 = I_2 + 2H_2O + SO_2.$$

This experiment forcibly illustrates the difference in stability between the compounds of chlorine and iodine with hydrogen, and consequently in the force with which they unite with that element.

123. Hydric iodide can be prepared in either of the following ways,—

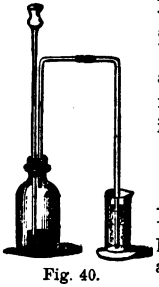


Fig. 40.

1. Powder some iodine, suspend it in water, and pass through the mixture a stream of hydric sulphide gas H_2S. The iodine unites with the hydrogen of that body and liberates the sulphur, which is precipitated as a yellowish-white powder, while the hydric iodide formed remains in solution in the water in which the iodine was suspended.

$$2I_2 + 2H_2S = 4HI + S_2.$$

Perform the operation as described, continuing the passage of the gas till the liquid becomes colourless and smells strongly of sulphuretted hydrogen ; boil until it has lost that smell, filter to remove the sulphur, and you have an aqueous solution of the acid body.

124. Another way to prepare the compound, especially appli-

cable when it is required in the gaseous form, is to act on phosphorous iodide (PI_3), with a small quantity of water—

$$PI_3 + 3H_2O = 3HI + H_3PO_3 \text{ (hydric phosphite).}$$

The operation is conducted so as to form the iodide of phosphorus at the same time that it is used. Into a small retort put one part of red phosphorus, just cover it with water, and add eight parts of iodine little by little,* applying a gentle heat. Iodide of phosphorus is first formed, and is immediately decomposed by the water present.

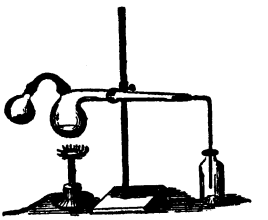


Fig. 41.

Hydric iodide comes off regularly in the form of a colourless gas, which fumes in moist air, even more strongly than hydric chloride. It can be collected by downward displacement, and the same experiments tried with it as with hydric chloride.

125. After having proved that it does not bleach; that it is very soluble in water, &c.; observe that it does *not* colour starch paste. Put some of its aqueous solution aside in an open vessel. In a few hours it will have become brownish, and acquired the power of rendering starch blue. As it is free iodine only which has this power, we conclude that some of that element is now uncombined with hydrogen, and that it has been liberated by the action of the oxygen of the air, which has combined with the hydrogen it was formerly in union with. This experiment shows how much less forcibly iodine holds hydrogen, even when it has got it, than chlorine does.

Mix a small quantity with starch paste, and add one drop of chlorine water to the colourless mixture, which will immediately turn blue. Add chlorine water in excess, the blue colour will disappear. For the chlorine

* A convenient arrangement for this purpose is shown in the figure. The iodine is placed in the little flask which is connected with the tubulus of the retort by a wide piece of caoutchouc tube, and is transferred to the retort as required by lifting the flask. This admits of adding successive small quantities without letting air in.

in this experiment, substitute a solution of "chloride of lime," or other readily reduced body—iodine will be liberated.

126. The metallic iodides are, as a rule, less soluble than the corresponding chlorides. Many of them have brilliant and characteristic colours, and, therefore, iodine in combination is very easily detected. The tests for it are—

1. As chlorine turns iodine out of its combinations with hydrogen and the metals, add to the liquid under examination some starch paste, and then a very little chlorine water. Be careful not to add too much of this re-agent, as an excess will destroy the blue colour first produced (this re-action serves either for soluble or insoluble iodides).

2. The body is to be heated in a test-tube, with a small quantity of binoxide of manganese and strong oil of vitriol. The production of violet vapours gives the required indication; this, like the last test, is applicable to all iodides.

3. Argentic nitrate, added to any acid *solution* containing an iodide, gives rise to the production of a yellowish precipitate of argentic iodide (AgI), which clots on agitation like the chloride, but differs from that body by its insolubility in ammonia, which only renders it white.

4. Plumbic acetate gives a bright yellow precipitate of plumbic iodide (PbI_2) which dissolves in a sufficient quantity of hot water, and crystallises out on cooling in magnificent golden spangles. This is very characteristic. (Note. In trying this experiment, add some free "acetic acid" to your acetate of lead solution.)

5. A solution of mercuric chloride, added to one containing a soluble iodide, gives at first a yellow precipitate, which turns in a few moments to a bright scarlet, if it is not dissolved by an excess of either mercuric chloride or of the iodide solution. This re-action, though very characteristic when obtained, is not adapted for the discovery of small quantities, as an excess of either re-agent dissolves the precipitate.

127. The iodides which are insoluble can be prepared by precipitation, and the soluble ones, like the corresponding chlorides, either by causing iodine to unite directly with the metal, or by dissolving the oxide or hydrate of the metal in solution of hydric iodide. Potassic iodide, which is largely used in medicine, is prepared in a rather different manner. Iodine is added to a solution of potassic hydrate until the liquid remains of a brown colour, after warming a little time,

$$6\,I + 6\,KHO = 5\,KI + KIO_3 + 3\,H_2O.$$

Here, as in the corresponding action of chlorine on potash, we have an oxygen salt formed. As the iodide is wanted alone, the whole liquid is evaporated to dryness, and fused at a high temperature in a porcelain crucible. By this operation, the excess of iodine which gave its colour to the mass is driven off, and then the oxygen of the iod*ate* goes, just as that of the chlorate does under similar circumstances. The iodide remaining is then crystallised. Prepare some of the salt by this method, and prove its freedom from iod*ate* by dissolving a little in water, adding starch paste and *very dilute* hydric chloride. If there is the least trace of iodate, a blue colour will be produced, because the oxygen of it will rob the hydric iodide formed of its hydrogen. The action of the hydric chloride on potassic iodide and iodate respectively, may be represented as

$$KI + HCl = KCl + HI$$
$$KIO_3 + HCl = KCl + HIO_3,$$

and the action of hydric iodate on hydric iodide as

$$HIO_3 + 5\,HI = 3\,H_2O + 3\,I_2.$$

OXIDISED COMPOUNDS OF IODINE.

128. If iodine be boiled with fuming hydric nitrate (HNO_3), which is a very powerful oxidising agent, it is converted into hydric iodate HIO_3, and this, if heated to a temperature of 170° C., loses water, and leaves iodic pentoxide—

$$2\,HIO_3 - H_2O = I_2O_5.$$

That free iodine is oxidised by hydric nitrate, and that the product is stable enough to bear drying so as to give an anhydrous product, is a remarkable illustration of the difference of the force with which iodine and chlorine combine with, and

hold oxygen. Another illustration of the same fact is afforded by this experiment—

Fuse some potassic chlorate in a porcelain crucible, and when it gives off oxygen freely, throw into the molten mass some powdered potassic iodide, previously heated in another small crucible: violent action ensues; so much heat is liberated as to make the mass glow faintly, and on dissolving the cooled mass in the smallest quantity of boiling water, and cooling, crystals of potassic *iodate* will be obtained, while potassic chloride will remain in solution. The potassic iodide is in fact burnt by the oxygen of the potassic chlorate.

Silver iodate $AgIO_3$ is insoluble.

129. Hydric periodate HIO_4 is known, and from it anhydrous per-iodic acid can be obtained by simply heating to 168°C.,

$$2\,HIO_4 = H_2O + I_2O_7.$$

Compare the above statements regarding the existence and preparation of I_2O_5 and I_2O_7 with those made about the corresponding chlorine compounds.

FLUORINE, Symb. F. Atomic weight 19.

Combining vol. = 1 = $\boxed{19}$ (hypothetical).

130. Fluorine is by no means so abundant as chlorine, but is pretty widely distributed in nature, always, however, in combination. Its most common compounds are fluor spar, which is fluoride of calcium (CaF_2), and cryolite, a fluoride of sodium and aluminium—$3\,NaF, AlF_3$.

Many of the mineral phosphates now so largely used for making artificial manures contain an appreciable amount of this element; and bones, teeth, the seeds of many plants, &c., have traces of it present. It can be liberated from its compound with silver, by the action of chlorine or iodine, but it attacks all things so powerfully, that it has hitherto been found impossible to ex-

amine its properties, since there is no material of which to make vessels for containing it. It has been said that when perfectly dry it does not attack perfectly dry glass, and that it is a colourless gas. But this is doubtful.

131. Though fluorine is little known, its hydrogen compound is prepared with ease, and has some important applications. When a metallic fluoride is distilled with hydric sulphate (oil of vitriol), the metal is replaced by hydrogen, by a reaction similar to that in the case of chlorides. As calcic fluoride

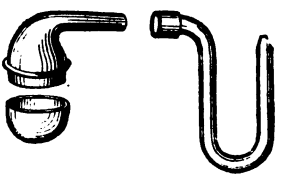


Fig. 42.

is the commonest fluoride, it is made use of. It is distilled together with hydric sulphate in a leaden or silver retort, the vapours given off are condensed in a tube of the same metal, and the resulting liquid preserved in bottles of lead or gutta-percha. The reaction is,

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

The *liquid* obtained by the reaction given, is in fact a very strong solution of hydrofluoric acid gas in water (derived from accidental moisture in the re-agents). By distillation with phosphoric pentoxide (P_2O_5), the water is removed and gaseous hydric fluoride obtained. Hydric fluoride is a colourless gas, which fumes strongly in the air, and is soluble in water to an almost unlimited extent. The gas and its solution are both very stable, even more so than hydric chloride.

Its composition by volume is *assumed* to be 1 volume of each of its constituents united without condensation, because it is so analogous to hydric chloride and iodide, which are *proved* to be

so constituted. As fluorine has not been isolated and the specific gravity of hydric fluoride even has not been determined (owing to its action on glass), there is no absolute proof that it has the volumetric composition assigned to it.

132. Its most characteristic and valuable property may be exhibited without taking the trouble to prepare its aqueous solution, by proceeding thus:

Into a common leaden ink-pot, put a pinch of coarsely powdered fluor spar, on to this pour three or four times its bulk of oil of vitriol (H_2SO_4); cover the pot with a piece of glass, and *very gently* warm the whole. After the lapse of five minutes you will find the glass is etched all over the part exposed to the fumes of hydrofluoric acid. Repeat the experiment, having first covered the glass with white wax and drawn some lines through the latter on to the glass, by means of a sharp point. The exposed portions of the glass will be etched or eaten away as before, but the wax will have protected the rest.* You can thus engrave any required pattern or writing on glass. This reaction also constitutes a very delicate test for the presence of a fluoride in any substance not containing silica.

Fig. 43.

An aqueous solution of hydric fluoride is sold, and is very useful in a laboratory for marking glass vessels. It is kept in bottles of gutta-percha, on which it has no action. As it produces very painful ulcers if allowed to fall on the skin, it is necessary to be careful in using it. Fluorides are prepared like the corresponding chlorides in most instances. Fluoride of silver is soluble. Fluorine forms no compound with oxygen.

* The action which causes this etching is explained in the chapter on silicon.

QUESTIONS ON CHAPTER VII.

1. Sketch the points of resemblance and difference of chlorine and bromine.

2. What are the sources of iodine? How is it prepared? Describe the properties of iodine. What is its vapour density?

3. How does iodine differ from chlorine in its relation to hydrogen?

4. What would be the weight of one litre of iodine vapour if it could be measured at 0° centigrade, and a pressure of 30 in. of mercury?—*Ans.* 11·34 grammes, nearly.

5. How can the presence of *free* iodine be detected?

6. Why cannot hydric iodide be prepared by the re-action analogous to that employed in the case of hydric chloride?

7. How can hydric iodide be prepared? (give both methods, with the equations representing them).

8. Describe the properties of hydric iodide.

9. What is the action of air and of chlorine, on its solution?

10. How is potassic iodide prepared?

11. How is the presence of a soluble iodide detected?

12. What is formed when iodine is boiled with fuming hydric nitrate? What change does it undergo if heated to 170° C.?

13. How is hydric fluoride prepared? What is its most valuable property?

14. If 55 cubic centimetres of gaseous hydric iodide were mingled with 50 cubic centimetres of chlorine, what re-action would occur, and what volume of gas would be left? What would the gas consist of?—*Ans.* Total volume remaining = 77·5 cubic centimetres, of which 22·5 are chlorine, and 55 are hydric chloride.

15. If 25 cubic centimetres of gaseous hydric iodide were completely decomposed by zinc, what volume of hydrogen would be obtained?—*Ans.* 12·5 cubic centimetres.

16. How would you proceed to detect the presence of a soluble (*a*) Chloride, (*b*) Iodide, and (*c*) Fluoride, present singly in a liquid?

17. Explain the liberation of iodine from hydric iodide by a solution of chloride of lime.

18. What weight of iodine would be liberated if excess of hydric chloride were added to a solution of 1 gramme of potassic iodate and an unlimited amount of potassic iodide?—*Ans.* 3·56 grammes, nearly.

19. What would be the volume of 10 grammes of hydric fluoride?—*Ans.* 5600 cubic centimetres.

20. How many cubic inches of hydrogen in 5 cubic inches of hydric fluoride?—*Ans.* 2·5 cubic inches.

21. On what grounds is our opinion, of the composition of hydric fluoride by volume, founded?

CHAPTER VIII.

RELATIONS OF THE THREE ELEMENTS, CHLORINE, BROMINE, AND IODINE.

133. CHLORINE unites with hydrogen and the metals more readily and more forcibly than bromine, and bromine more than iodine.

For instance: 35·5 parts of chlorine uniting with 32·5 parts of zinc produce the evolution of 50,685 units of heat,* but 80 parts bromine uniting with the same quantity of metal, only give 40,640, and 127 of iodine but 26,617. Or, to give substance to these numbers: If 35·5 grammes of chlorine combine with 32·5 grammes of zinc, so much heat will be evolved as will be capable of raising 50,685 grammes of water from 0° C. to 1° C.; but 127 grammes of iodine, on uniting with 32·5 grammes of zinc, will only raise 26,617 grammes of water from 0° C. to 1° C.

Now the amount of heat evolved is a measure of the chemical energy of the combination. When a chemical decomposition takes place, as much heat is absorbed as was evolved on the original combination. If a chemical combination and a decomposition take place at the same time, and the combination occurs with the greater energy (which it mostly does in observable cases), there will be heat evolved equal to the *difference*. Therefore, if 35·5 grammes of chlorine decompose the product of the union of 127 grammes of iodine with 32·5 grammes of zinc, the heat evolved will be sufficient to raise 24,068 grammes of water from 0° C. to 1° C., for $50685 - 26617 = 24068$.

* A unit of heat is that quantity of heat which is capable of raising a unit weight of water 1° Centigrade of temperature.

Dissolve about half an ounce of potassic iodide in its own weight of water in a small beaker stood in a large pan of cold water; in the same pan of water stand a bottle of bromine. Let both remain for an hour to acquire the same temperature. Immerse the bulb of a delicate thermoscope in the solution of iodide, mark the point at which the liquid in your thermoscope stands, then add a few drops of bromine at a time, taking care not to add so much as to cause a *permanent* precipitate of iodine. A considerable rise of temperature will take place.

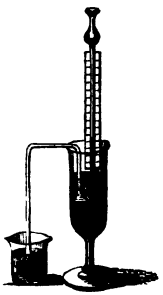


Fig. 44.

If a solution of a bromide be in the same way decomposed by chlorine water, a rise of temperature will also result, but will not be so marked, as the chlorine is not in so concentrated a form, and we are forced to add a great quantity of water with it. This added water absorbs much of the heat. Observe that not only does chlorine turn out of their combinations both bromine and iodine, and bromine turn out iodine, but that when the change takes place heat is evolved, showing that the ejecting element combines with the metal (or hydrogen) present with more energy than the one thrown out.

In the thermoscope shown in the fig. 44, the expansion of the air in the terminal bulb causes the coloured water in the bend to rise in the upright stem, which is furnished with an arbitrary scale, and which is open at the top. The bulb at the bend is kept immersed in water to prevent it being warmed by handling. An ordinary chemical thermometer serves, if the experiment is to be exhibited to two or three persons only.

134. With oxygen, on the other hand, these elements have relations in inverse order to those with hydrogen. The energy of combination of iodine with oxygen is greater than that of bromine, and that of the latter than that of chlorine. When fused potassic iodide was added to potassic chlorate, heat was evolved, and potassic iodate formed, the chlorine being deprived of its oxygen by the iodine. Another illustration of this point is afforded by heating together powdered iodine and potassic chlorate, when a dark brown liquid having the composition I Cl

distils out, and potassic iodate remains behind. The reaction giving rise to these products may be represented as

$$I_2 + K Cl O_3 = K I O_3 + I Cl,$$

i. e., one atom of the molecule of iodine turns out and takes the place of the chlorine of the chlorate, while the other atom unites with the chlorine so liberated. (Other bodies result at the same time from the decomposition of some of the potassic chlorate by the heat.)

135. The stability of the compounds which these elements form with hydrogen is greatest in the case of chlorine,* hydric chloride being *very slowly* decomposed by oxygen in presence of water, even under the influence of strong sunlight, and not at all acted on by strong hot hydric sulphate. Indeed, chlorine decomposes water under the influence of light, taking its hydrogen to form hydric chloride and setting its oxygen free;

$$2 Cl_2 + 2 H_2 O = 4 H Cl + O_2.$$

Hence the reason for keeping chlorine water in a dark place. Hydric bromide loses its hydrogen slowly and incompletely by exposure to air, and is in considerable part destroyed by the oxidising action of strong hydric sulphate. Hydric iodide is rapidly and completely decomposed by air, strong hydric sulphate, and even weaker oxidising agents.

It is worth observing that the atomic weight of bromine (80) is very nearly the mean of the atomic weights of chlorine and iodine $\frac{35{\cdot}5 + 127}{2} = 81{\cdot}25$, and that in all its chemical characteristics it lies between the two.

* The consideration of fluorine is omitted, because it is less studied, and appears not wholly to belong to this group.

CHAPTER IX.

SULPHUR, SELENIUM, AND TELLURIUM.

136. THE group of elements, the members of which unite with two atoms of hydrogen, consists of oxygen, sulphur, selenium, and tellurium.

Oxygen has been already considered; selenium and tellurium are too rare to engage our special attention; sulphur therefore will be the only one now treated of.

SULPHUR, Symbol = S. Atomic Weight 32

Combining volume 1 or $\boxed{32}$ $\left.\begin{matrix}S\\S\end{matrix}\right\}$ = 2 vol.

Like oxygen this element occurs in the free state, but is by no means so abundant. In the rocks of volcanic districts it is found filling small cavities, sometimes beautifully crystallised, at others only crystalline. It is also found in combination with metals, forming the large classes of "Blendes" and "Pyrites," such as iron pyrites ($Fe S_2$), copper pyrites ($Fe S_2)_n + (Cu S)_m$, zinc blende (Zn S), and galena, or lead blende (Pb S).

Metallic sulphates, which are very common, also contain sulphur, though they do not furnish a source of the element.

137. The sulphur, or brimstone of commerce, is nearly all obtained from the rocky bodies which contain it in the free state. Heat is applied to the mass containing sulphur, either by means of a fire of wood or by setting one part of the sulphur alight to melt the rest. The sulphur obtained by this first process is very impure. It is purified by *distilling* it from large iron or earthen

retorts, and condensing the vapour either slowly or quickly, according to whether it is wanted in the state of liquid or as powder. In the first case it is passed into a smallish earthen receiver, not kept very cold, where it condenses into a liquid, which is poured out into cylindrical wooden moulds, in which it solidifies to form the roll sulphur or brimstone of commerce. In the second case a large cold brick chamber receives the vapour, which condenses rapidly as a fine mealy powder known as flowers of sulphur.

138. Sulphur is sometimes prepared by heating "iron pyrites" $Fe S_2$ (out of contact with air), which gives up one-third of its sulphur,

$$3 Fe S_2 = S_2 + Fe_3 S_4,$$

just as the binoxide of manganese gives up one-third of its oxygen by the action of heat.

Heat about fifty grains of powdered iron pyrites in a test tube of hard glass, the mouth of which is loosely stopped by a cork or the finger. Reddish-yellow drops of fused sulphur will collect in the upper part of the tube and there solidify into yellow cakes.

139. Sulphur is a yellow solid, which conducts heat and electricity *very* badly, and which is so inelastic that when a stick of "brimstone" is held in the hand, it often splits into bits because the heat causes the outside to expand and wrench itself away from the still unwarmed interior portions. The splitting is accompanied by a characteristic crackling sound. It is insoluble in water, but soluble in carbonic disulphide ($C S_2$) and in oil of turpentine, It is almost exactly twice as heavy as water, bulk for bulk. It melts at 120° C., and boils at about 440° C.

139 A. When the vapour density of sulphur is determined by the method described in connection with iodine (§ 118), the temperature employed to vaporise the sulphur being 500° C., which is 60° C. above its boiling point, it is found to be 96 times as heavy as hydrogen. This fact taken alone would lead to the conclusion that the atomic weight of sulphur was 96, or its molecular weight was 192. But if the experi-

ment is made at a temperature of 1000° C., the vapour of sulphur is found to be only 32 times as heavy as an equal bulk of hydrogen at the same temperature, or its atomic weight is 32, and its molecular weight 64.

140. The action of heat on sulphur is peculiar, and the student should verify the following statements concerning it by performing the experiments described upon about half a pound of common brimstone.*

Place it in a deep-shaped porcelain basin bedded in sand contained in a much larger one. Apply heat gently to the outer basin, until all the sulphur is melted. Observe that it forms a very fluid liquid of a pale straw colour. remove the lamp, cover the basin with a glass plate, and watch for the point at which the surface of the fused mass becomes covered with a crust. Pierce two holes through the crust, one near the edge of the basin, the other opposite to it, and rapidly pour the fluid portion out through one of these holes into a Florence flask. With a stout knife cut round the crust about three-quarters of an inch from the edge and lift it out.

Its under surface and the sides of the basin will be found covered with long shining crystals of sulphur, belonging to the *oblique prismatic* † form. These are transparent at first, but become opaque in the course of a few days, from the production of a number of minute fissures during the change of these *oblique prismatic* crystals into a number of smaller *octahedrons* belonging to the *right prismatic* system, the most common form of sulphur. The needle-shaped crystals melt at 120 °C., and have a specific gravity of 1·98.

141. The portion of sulphur in the flask is now to be again heated till it melts, and, even then, the application of heat continued.

As the mass gets hotter it gets darker in colour, and at the same time thicker, till at about 200° Centigrade it is so thick (viscid) that it cannot be poured out without giving it some time to run. Indeed, it looks much like very thick treacle. If the heat be increased to about 240° Centigrade, the mass becomes more fluid, though not as liquid as at first, but retains its brown colour even when heated to its boiling point, 440° Centigrade. Pour some of the sulphur which has nearly reached the

* Half an ounce will suffice to show everything but the crystallisation.

† See Crystalline Systems—System 5.

boiling point into cold water to cool it suddenly, and leave the rest in the flask, observing it from time to time as it cools.

The portion poured into water will be found not to have hardened, but to have been converted into a more or less transparent mass of elastic strings. This plastic sulphur returns to the ordinary form in the course of a few hours, or instantaneously if plunged into boiling water. The portion of viscid sulphur allowed to cool slowly, returns to the ordinary form after passing through the same changes it underwent on heating, only in the reverse order.

142. Ordinary roll sulphur and the crystals obtained by cooling fused sulphur, or rather the opaque mass produced by the spontaneous change of the last, are both soluble in carbonic disulphide (CS_2); but the plastic sulphur is not so.

Shake up flowers of sulphur with carbonic disulphide, taking great care that no flame is within several yards of you at the time, and also to avoid inhaling much of the vapour of the bisulphide, the vapour of which is very explosive when mixed with air, and very poisonous. About three-quarters of the flowers of sulphur will be dissolved; filter off that portion which remains solid, put the clear liquid in a flask, and stand it aside uncorked, so that the solvent may evaporate slowly.

Crystals of great beauty will be gradually deposited, having the form of native sulphur, *i.e.*, the octahedron of the right prismatic system.* They melt at 114·5° C. and have a specific gravity of 2·05. As sulphur crystallises in forms belonging to two distinct *systems*, and not merely in two different forms of the same system, it is said to be *dimorphous* (two-formed). The plastic form of sulphur is insoluble in carbonic disulphide, and in other ways differs chemically and physically from the crystallised kind; it is therefore said to be an *allotropic* form of sulphur.

143. Sulphur, like oxygen, unites directly with most metals and metalloids, to form sulphides. In most cases these sulphides have formulæ analogous to the oxides formed by the direct union of oxygen with the same element. As sulphur at ordinary temperature is a solid, it is necessary to bring it into

* See Crystalline Systems—System 4.

the gaseous state, by heat, before comparing its actions with those of oxygen.

144. If a mixture of gaseous sulphur and hydrogen be exposed to a red heat, the two unite pretty readily to form hydric sulphide, (H_2S).

Pass pure dry hydrogen gas into one end of a three foot length of combustion tube, having placed a few lumps of sulphur near the end at which the gas enters. Push one or two plugs of cotton-wool into the other end; heat six or eight inches of the tube next the sulphur to redness by glowing charcoal, and while keeping up a steady current of gas, gradually melt, and then volatilise some of the sulphur.

Its vapour will partly combine with the hydrogen as the two pass through the heated part. The portion of vapour remaining uncombined will condense in the cool part of the tube, and those portions which take the form of flowers of sulphur from rapid cooling, will be caught and filtered off from the gas by the cotton plugs. A strong smell of rotten eggs will render manifest the production of sulphuretted hydrogen.

145. In comparing together oxygen and sulphur, let us next see whether other things besides hydrogen will burn in it when in the form of gas.

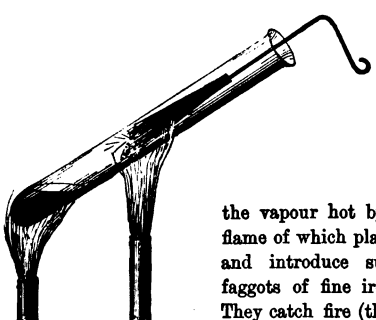


Fig. 45.

Heat some sulphur in a test tube, supported by a clip, until it boils. Keep the vapour hot by means of another lamp, the flame of which plays on the middle of the tube, and introduce successively small brushes or faggots of fine iron and copper wire (fig. 45). They catch fire (the iron only after being made very hot) and burn, producing *sulphides* of iron and copper. Sheet copper, lead, zinc, &c., may be used in place of the wire, if thin and cut into strips. Carbon burns in vapour of sulphur to form CS_2, carbonic disulphide (q. v.).

Observe that sulphur resembles oxygen in all these properties.

HYDRIC SULPHIDE, HYDROSULPHURIC ACID.

SULPHURETTED HYDROGEN.—Symb. H_2S, molecular weight 34.

Combining vol. | 17 | 17 |.

146. The compound of sulphur with hydrogen, as before mentioned, has a formula analogous to that of water.

$\left.\begin{matrix}H\\H\end{matrix}\right\}O$, hydric oxide, $\left.\begin{matrix}H\\H\end{matrix}\right\}S$, hydric sulphide.

Like that body, it is procurable by the direct combination of its constituents, both being in the free state. Nascent hydrogen likewise unites with nascent sulphur, as it does with nascent oxygen, to give in this case sulphur water (?) instead of oxygen water. Compare the following actions:—

$$Zn + H_2SO_4 = H_2 + ZnSO_4,$$
$$ZnO + H_2SO_4 = H_2O + ZnSO_4,$$
$$ZnS + H_2SO_4 = H_2S + ZnSO_4,$$

147. It is by the last reaction that sulphuretted hydrogen is most commonly prepared in practice—only, instead of the sulphide of *zinc* we use that of iron (FeS):

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

Lumps of ferr*ous* sulphide * are to be put into such a bottle as is used in the preparation of hydrogen, then covered with water and acted on by hydric sulphate or chloride, added little by little through the funnel. A gas is given off, which may be collected by downward displacement, or over *hot* water.

As the ferrous sulphide always contains free iron, the gas prepared from it always contains free hydrogen. When pure hydric sulphide is required, it is advisable to substitute anti-

* Prepared by throwing a mixture of 7 parts of iron turnings and 4 parts sulphur into a red-hot crucible, and heating for a short time in a fire. Iron pyrites, FeS_2, will not serve, as it is not dissolved by dilute hydric sulphate or chloride.

monic tersulphide, Sb_2S_3, for the ferrous sulphide, and strong "muriatic acid" for dilute hydric sulphate; but as in this case heat is required to effect the reaction, it is necessary to use the apparatus employed for preparing hydric chloride (§ 72):

$$Sb_2S_3 + 6\,HCl = 2\,SbCl_3 + 3\,H_2S.$$

148. Burn the gas, dried by passing over chloride of calcium (not oil of vitriol), from a jet placed under the tube used to show that water is formed by the combustion of hydrogen (§ 36).

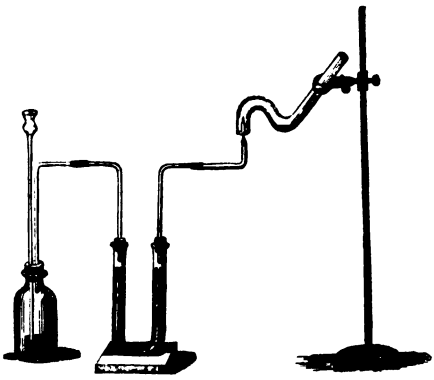


Fig. 46.

It gives a very *blue* flame; water condenses in the tube, but instead of being neutral and odourless, it is strongly acid, and smells of burning sulphur, because the sulphur in the original gas has combined with oxygen, and the product of that combination (SO_2), sulphuric dioxide, has partly condensed along with the water formed at the same time:

$$2\,H_2S + 3\,O_2 = 2\,SO_2 + 2\,H_2O.$$

149. Pass some of the dry gas through a piece of hard quill tubing kept red hot by a lamp; it will be partly decomposed, and sulphur deposited beyond the flame.

Observe, that though heat causes sulphur and hydrogen to

unite, it also causes them, under other circumstances, to separate, as it does oxygen and hydrogen, and with greater ease too.

150. Pass the gas through a tube containing ignited iron filings. Sulphide of iron will be formed, as oxide of iron is in the corresponding experiment with steam, and hydrogen will be set free (§ 35). The formation of sulphide of iron may be proved by dissolving the contents of the tube in dilute hydric sulphate, when the smell of sulphuretted hydrogen will be perceived.

151. Fill a bottle with the gas, open its mouth under water, let a few bubbles escape, close the bottle, and agitate the remaining gas with the water which has entered. In this way prove that sulphuretted hydrogen is soluble in water.

Observe, that the solution made thus (or by passing a stream of the gas into water), has the smell and taste of the gas, and a slight acid reaction to litmus paper.

152. Expose some of the solution to the air in a small flask during two or three days, till all smell has disappeared. Sulphur will be deposited. What does this show?

Add chlorine water to a portion; sulphur will be thrown down. Explain the reaction.

Bring together sulphuretted hydrogen and sulphuric dioxide (SO_2) either in the gaseous state or dissolved in water. Sulphur will be deposited:

$$4H_2S + 2SO_2 = 4H_2O + 3S_2.$$

The last reaction affords a ready method of destroying any sulphuretted hydrogen which may have escaped into the air of a room. It is only necessary to burn a small piece of brimstone.

153. The other properties of sulphuretted hydrogen are mostly of such a kind as to be beyond proof by experiment by the student. It is condensible into a *very* mobile liquid by cold and pressure, and this liquid can be frozen into a clear ice-like solid by exposure to an extremely low temperature. One volume of cold water dissolves about three times its volume of the gas. It is excessively poisonous.

154. Sulphuretted hydrogen is much used in the laboratory in the course of analysis, for when brought in contact with most metallic solutions under appropriate conditions, its sulphur unites

with the metal to form a sulphide, which, being insoluble in the liquid, is precipitated.

** To a solution of arsenic trioxide (As_2O_3), made acid by hydric chloride, add sulphuretted hydrogen water. A yellow precipitate of arsenic tersulphide (As_2S_3) is formed :

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O.$$

To this precipitate add potash or ammonia in quantity sufficient to render it alkaline ; the precipitate dissolves. Observe, that it is only when the liquid is acid that arsenious sulphide can be precipitated.

Antimony and tin, gold and platinum solutions behave like arsenic ones in this respect. Antimony, however, gives an orange precipitate, and tin a brown, or dirty yellow one. Try the same reactions with salts of copper, lead, mercury, silver,* or bismuth. It will be found in each case that a precipitate is formed (black or brown), which is *not* soluble in alkalies, and which is, therefore, produced either in alkaline or acid solutions.

Again, use a solution of iron, cobalt, nickel, manganese, or zinc. No precipitate will be formed if the solution be acid with hydric chloride ; but if ammonia be added, a precipitate of the sulphide of the metal will be formed—iron, cobalt, and nickel giving fine black ; manganese, flesh-coloured ; and zinc, white precipitates. The other metals (common ones), give no sulphides in presence of water, or only soluble ones. Metals are thus divided into four groups by this reagent.

155. As sulphuretted hydrogen is used to detect the presence of a metal, a metallic solution may be used to detect the presence of sulphuretted hydrogen. Paper soaked in acetate of lead solution is usually employed for this purpose ; it is turned brown by the least trace of the gas.

156. As mentioned in § 145, sulphur forms a number of sulphides analogous in composition to the oxides ; but there are oxides known which have no sulphur representatives, and sulphides which are not matched by oxides. We will here give a list of oxides and sulphides in parallel columns, representing each as derived from hydric sulphide and hydric oxide (water) respectively. As these two bodies (H_2S and H_2O) contain two

* In the case of silver you must not acidulate with hydric chloride. Why ?

atoms of hydrogen, we can, in some cases, obtain two different sulphides or oxides of the same metal, each containing only one atom of sulphur in the molecule.

Sulphides and oxides of metals which are monovalent, *i.e.*, are equal in combining power to *one* atom of hydrogen :

Oxides formed on the type	Sulphides formed on the type
$\left.\begin{matrix}H\\H\end{matrix}\right\}$ O, water.	$\left.\begin{matrix}H\\H\end{matrix}\right\}$ S, hydric sulphide.
$\left.\begin{matrix}K\\H\end{matrix}\right\}$ O, hydropotassic oxide, or potassic hydrate.	$\left.\begin{matrix}K\\H\end{matrix}\right\}$ S, hydropotassic sulphide, or potassic sulph-hydrate.
$\left.\begin{matrix}K\\K\end{matrix}\right\}$ O, potassic oxide, or anhydrous oxide of potassium.	$\left.\begin{matrix}K\\K\end{matrix}\right\}$ S, potassic sulphide, or sulphide of potassium.
$\left.\begin{matrix}Na\\H\end{matrix}\right\}$ O, hydrosodic oxide, or sodic hydrate.	$\left.\begin{matrix}Na\\H\end{matrix}\right\}$ S, hydrosodic sulphide, or sodic sulph-hydrate.
$\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}$ O, argentic oxide, or oxide of silver.	$\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}$ S, argentic sulphide, or sulphide of silver.

Observe that we may have either one or both atoms of hydrogen in our *type* replaced by its *equivalent* of metal, also that the names of the bodies represent their composition. The names potassic hydrate and sodic hydrate are verbal expressions which represent one view of the constitution of the bodies to which they are applied. This view represents them as consisting of the metal, say potassium, united with the radicle (root ; base) of water, called hydroxyl. They are then written as K (H O), or Na (H O), H O being called a compound radicle, and considered as the chemical equivalent or representative of chlorine in the chlorides.

K Cl, potassic chloride. K (HO), potassic hydrate.

157. The above oxides, of the formula M_2O, with the exception of that of silver, can be made by the direct union of oxygen with the metal.

Expose some thin slices of sodium to the dry air above the surface of oil of vitriol confined under a bell jar. They will be converted into a white brittle mass of Na_2O. The corresponding sulphides can be formed by heating the metal and sulphur together in atomic proportions.*

* K_2S and Na_2S have not been obtained in a state of isolation and perfectly pure.

Heat a fragment of sulphur in a test-tube, and put in some silver leaf, black sulphide of silver will be immediately formed.

158. When the before-mentioned anhydrous oxides are acted on by water they give the hydrates (excepting silver), *e. g.* ;—

$$K_2O + H_2O = 2\,K\,HO,$$

i. e., one atom of potassium changes places with one of hydrogen.

Similarly the sulphides, when treated with sulphuretted hydrogen, give the sulphydrates,

$$K_2S + H_2S = 2\,K\,HS.$$

For other modes of preparation and the properties of sulphides, larger works must be consulted.

159. The divalent metals form oxides and sulphides by replacing all the hydrogen in one molecule of water or hydric sulphide respectively, in forming what are considered their principal oxides and sulphides, but most of them form more than one compound.

$\left.\begin{matrix}H\\H\end{matrix}\right\}$ O.	$\left.\begin{matrix}H\\H\end{matrix}\right\}$ S.
Ca″ O, calcic oxide, or lime.	Ca″ S, calcic sulphide.
Ba″ O, baric oxide, or baryta.	Ba″ S, baric sulphide.

These oxides and sulphides, when treated with water and hydric sulphide respectively, yield hydrates and sulphydrates:—

$$Ba''\,O + H_2O = Ba''\,(HO)_2 \text{ corresponding to } Ba''\,Cl_2.$$
$$Ba''\,S + H_2S = Ba''\,(HS)_2 \quad \text{ditto} \quad \text{ditto.}$$

Ba″ O_2, baric dioxide.	Ba S_2 (?), baric disulphide.
Zn″ O, zinc oxide.	Zn″ S, zinc sulphide.
Cu″ O, cupric oxide.	Cu″ S, cupric sulphide.
Cu''_2O, cuprous oxide.	Cu_2 S, cuprous sulphide.
Hg″ O, mercuric oxide.	Hg″ S, mercuric sulphide.
Hg_2 O, mercurous oxide.	Hg_2 S, mercurous sulphide.
Pb O, plumbic oxide.	Pb″ S, plumbic sulphide.
Pb_3O_4, plumboso-plumbic oxide.	
Pb O_2, plumbic dioxide.	
Mn″ O, manganous oxide.	Mn″ S, manganous sulphide.
Mn_3O_4, manganoso-manganic oxide.	Sulphur compound wanting.
Mn_2O_3 } manganic oxide. sesquioxide of manganese.	,, ,, ,,

$Mn\ O_2$, manganic dioxide.	Sulphur compound wanting.
* $Mn\ O_3$ { manganic trioxide. manganic acid.	,, ,, ,,
* $Mn_2\ O_7$ { manganic heptoxide. per-manganic acid.	,, ,, ,,
$Fe\ O$, ferrous oxide.	$Fe\ S$, ferrous sulphide.
Fe_2O_3, ferric oxide (sesquioxide of iron).	$Fe_2\ S_3$ (?), ferric sulphide, sesquisulphide of iron.
Fe_3O_4, ferrosoferric oxide.	$Fe_3\ S_4$, ferrosoferric sulphide.
$Fe\ O_2$ wanting.	$Fe\ S_2$, ferric disulphide.
* $Fe\ O_3$, ferric trioxide, ferric acid.	Sulphur compound wanting.

These show that the same metal may combine with many different quantities of oxygen and sulphur. Those compounds marked * are only known in combination.

160. Examples of oxides and sulphides of trivalent metals. As these metals in most cases replace three atoms of hydrogen, they must do it in three molecules of water or of hydric sulphide, as that quantity is the least which contains a quantity of hydrogen divisible by three :—

$\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}\ O_3$, water (three molecules).	$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}\ S_3$, hydric sulphide.
$\left.\begin{matrix}Au'''\\Au'''\end{matrix}\right\}\ O_3$, auric oxide, oxide of gold.	$\left.\begin{matrix}Au'''\\Au'''\end{matrix}\right\}\ S_3$, auric sulphide, sulphide of gold.
$\left.\begin{matrix}Bi'''\\Bi'''\end{matrix}\right\}\ O_3$, bismuthic oxide.	$\left.\begin{matrix}Bi'''\\Bi'''\end{matrix}\right\}\ S_3$, bismuthic sulphide.

But there are other oxides and sulphides belonging to the metals of this group, *e. g.* :—

$$As_2\ O_5 \qquad As_2\ S_3 \qquad Sb_2\ S_5, \text{ \&c.}$$

161. The tetravalent metals form oxides and sulphides by replacing four atoms of hydrogen in two molecules of water, or sulphuretted hydrogen :—

$Sn^{iv}\ O_2$, stannic oxide.	$Sn^{iv}\ S_2$, stannic sulphide ;
but these are also known :—	
$Sn\ O$, stannous oxide, and	$Sn\ S$, stannous sulphide.

Observe that when a metal forms more than one compound with oxygen or sulphur, that one which contains most oxygen or sulphur has its name ending in *ic*, and the other in *ous*, as in the

case of the chlorine oxides, unless the proportion of the oxygen or sulphur is indicated by a numeral prefix.

162. Sulphur forms another compound with hydrogen besides H_2S, it is supposed to have the composition H_2S_2, and to correspond to peroxide of hydrogen (H_2O_2), which it resembles in many of its reactions. Peroxide of hydrogen being considered as HO, HO, persulphide of hydrogen will be HS, HS; and as we have seen we have sulphydrates corresponding to the hydrates.

163.** Sulphur with chlorine.

The compounds of these two elements are of small importance. Two only are known in a state of purity, viz. :—

Cl_2S, protosulphide of chlorine, corresponding to Cl_2O, protoxide of chlorine, and

Cl_2S_2, bisulphide of chlorine, analogous in composition to the unknown binoxide.

Both of these bodies are made by causing chlorine to unite directly with sulphur—in the first case employing an excess of chlorine, and in the other an excess of sulphur. Both are decomposed by water. They may also be regarded as the products of the replacement of hydrogen in H_2S and H_2S_2 by chlorine.

OXIDISED COMPOUNDS OF SULPHUR.

164. Sulphur forms only two oxides.

SO_2, sulphuric dioxide, or sulphurous acid gas.

SO_3, sulphuric trioxide, or anhydrous sulphuric acid.

Sulphur, as is well known, burns readily with a pale blue flame, and production of a peculiar choking smell popularly known as that of brimstone. If sulphur is burnt in a known volume of oxygen and the resulting gas measured at the initial temperature, it will be found that no alteration of volume has taken place; therefore the body formed contains its own volume of oxygen. If then the specific gravity of the body be taken, it will be found to be 2·19, which is sensibly equal to twice that of oxygen (1·088), therefore it contains equal weights of sulphur and oxygen combined. In two absolute volumes ($11·2 \times 2$ litres) therefore there must be 2×16 grammes of oxygen and 32 grammes of sulphur, so the formula for it is SO_2.

165. For use in the laboratory sulphuric dioxide is most commonly made by taking away oxygen from hydric sulphate H_2SO_4, by some body having a great tendency to combine with that element. Hydrogen and sulphur will equally serve the purpose, as also will carbon. The hydric sulphate must be concentrated and hot, or it will not give up oxygen to any of these. Hydrogen employed in the nascent state, *i. e.*, before two

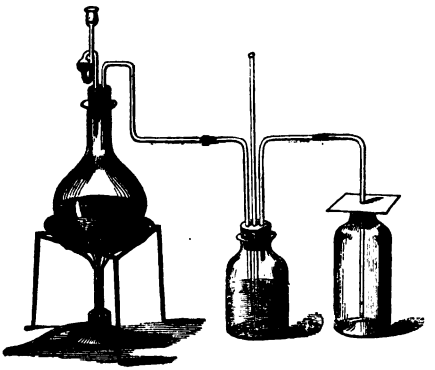


Fig. 47.

atoms of it have united to form a molecule, is best adapted for the purpose. The operation is conducted thus :—

166. Into the flask of an apparatus such as is employed for the preparation of chlorine, put two or three ounces of copper turnings or mercury, cover them with concentrated oil of vitriol and apply heat. Fig. 47.

Sulphuric dioxide will be given off, and a sulphate of the metal formed.

$$Hg + 2\,H_2SO_4 = HgSO_4 + 2\,H_2O + SO_2$$
$$Cu + 2\,H_2SO_4 = HgSO_4 + 2\,H_2O + SO_2.$$

167. The gas as it comes off may be collected by downward displacement, as it is more than twice as heavy as air.

$S = 32 = 1$ volume
$O_2 = 32 = 2$ volume
$SO_2 = 64 = 2$ volume $\therefore$ one volume $= 32$;

and as one volume of air $= 14{\cdot}4$, SO_2 : Air :: 32 : 14·4.

168. The reaction which takes place may be represented as, first, the replacement of two atoms of hydrogen by the divalent copper (or mercury) in one molecule of hydric sulphate.

$$Cu + H_2SO_4 = H_2 + CuSO_4;$$

and secondly, the subsequent, or rather simultaneous combination of that hydrogen with an atom of oxygen from the remaining molecule of hydric sulphate, which by loss of this oxygen is reduced to hydric sulphite H_2SO_3, which in its turn is split up by heat into water and sulphuric dioxide:—

$$H_2SO_4 + 2H = H_2O + H_2SO_3, \text{ and}$$
$$H_2SO_3 = H_2O + SO_2.$$

It is to be noted however that the reaction admits of another explanation, which is that the *metal* takes oxygen from one portion of the hydric sulphate, and the oxide so produced reacts on the remainder, thus $CuO + H_2SO_4 = CuSO_4 + H_2O$. But as metals, such as zinc and iron, dissolve in hydric sulphate too dilute to exert an oxidising action, with evolution of hydrogen, and yet if the strength of the acid be increased give sulphurous acid gas, it is more probable that the first explanation is the correct one. Moreover, there is always some cupric sulphide, Cu S, formed, which can only be explained by supposing the action described in § 177 to take place, and the hydric sulphide so produced to react on the cupric sulphate present.

169. If sulphur is boiled with concentrated oil of vitriol till action ceases, it takes oxygen from it in such proportion that all the sulphur, both of the oil of vitriol itself and that added, is converted into its dioxide, *if* the two are in the proportions represented in the first half of

$$4H_2SO_4 + S_2 = 4H_2O + 6SO_2.$$

If either body be in excess, some of it will remain unacted on. This method, which shows so favourably on paper, is inconvenient in practice; because the sulphur melts into globules exposing so small a surface that the action is very slow.

When crushed charcoal (carbon) is heated with oil of vitriol, sulphuric dioxide is given off very readily and abundantly, but

mixed with carbonic dioxide. The reaction which takes place is quite similar to that where sulphur is employed,

$$4\,H_2SO_4 + C_2 = 4\,H_2O + 2\,CO_2 + 4\,SO_2,$$

only the reducing agent (the carbon in this case) yields CO_2, instead of an additional molecule of SO_2. If the gas (SO_2) is only required for preparing its solution, or the alkaline sulphites, this method is the most convenient and economical.

170. Collect several narrow-mouth stoppered bottles of the gas, and prove that it possesses,—

1st. An acid reaction.
2nd. That it is soluble in water.
3rd. That it neither burns or supports combustion.
4th. That it is heavier than air.

171. Put a moistened red rose into a bottle of the gas; in a few hours it will be bleached. Remove the flower, and throw it into some *very dilute* hydric sulphate or chloride. The colour will be restored after a time. Many other vegetable colours are also slowly bleached in the same way, as can be shown by passing the gas into decoctions of violets, red cabbage, logwood, &c. The addition of acid bodies to these bleached solutions renders most of them red, and the addition of alkalies, such as potash or soda, turns them green or purple.

Observe, the colour is not destroyed as it is by chlorine, but only converted into some new compound, which is again split up by an acid, or alkaline reagent.

This bleaching power of the gas is much made use of in the arts, for whitening those substances, such as straw, wool, silk, feathers, &c., which are injured by chlorine. It is made for these purposes by burning "brimstone."

172. Prepare a solution of the gas in water by passing it from the evolution apparatus into cold water as long as any is absorbed, and reserve the liquid for future use. As the gas dissolves heat is evolved, the liquid becomes slightly heavier, and acquires the smell, taste, and acid properties of the gas itself, and when saturated contains about 40 times its volume of the gas. By prolonged boiling the whole of the gas can be expelled from its solution. When cooled to 0° C. a saturated solution is said to deposit crystals, having the composition $H_2SO_3 = (H_2O, SO_2)$.

173. Pass some quantity of the gas prepared by help of copper or mercury, and which has been dried by chloride of calcium, into a U tube, which has both limbs strangulated (*i. e.*, drawn out so as to be very narrow), and which is kept surrounded by a freezing mixture of ice and salt, as shown in fig. 48.

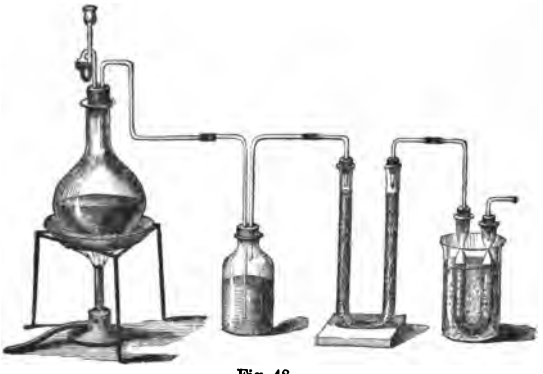


Fig. 48.

The gas will condense into a very mobile colourless liquid, which can only be preserved at ordinary temperatures by sealing the tube at the contracted portions by the blowpipe. Observe, that sulphuric dioxide is a gas at ordinary temperatures, but that by cooling it condenses into a liquid.

174. Open one point of a tube containing liquid sulphuric dioxide, which is at the temperature of the air, by holding the fine drawn out extremity in a gas flame till the pressure inside blows a hole through the softened glass. A violent rush of gas takes place, showing that the pressure inside the tube is great; and immediately the liquid boils violently, and continues to do so till all has again become gaseous, at the same time a very great reduction of temperature will take place.

Observe, that pressure on the surface of the liquid prevents it becoming a gas at temperatures which would otherwise keep it aëriform. In many instances it is found that simply compressing a gas to a great extent will cause it to liquefy.

175. It was mentioned in § 172, that the body H_2SO_3 exists. It is called hydrated sulphurous acid, or better, hydric sulph*ite*. Both atoms of hydrogen in it are replaceable by metals to form metallic sulphites, which can be prepared by precipitation if

they are insoluble in water, as most are, or by the direct action of sulphurous acid gas on the hydrate of the metal.

Divide a portion of solution of sulphuric dioxide into two equal parts. To one add solution of sodic hydrate, little by little, until the liquid is quite neutral, then evaporate and crystallise. A colourless body having the composition Na_2SO_3 will be obtained, and on testing will be found quite neutral.

$$2\,NaHO + \underbrace{H_2SO_3}_{\text{hydric sulphite.}} = Na_2SO_3 + 2H_2O.$$

Dissolve the crystals together with the mother liquid in more water, and add the other portion of the acid solution, and again crystallise.

These crystals are acid, and have the composition $HNaSO_3$, that is, hydric sulphite with only half the hydrogen replaced by sodium.

H_2SO_3 = hydric sulphite, or more fully, di-hydric sulphite.
$HNaSO_3$ = hydrosodic sulphite.
Na_2SO_3 = sodic sulphite, or disodic sulphite.

176. Add to a solution of sodic or potassic sulphite a solution of baric chloride, or lead acetate, you will obtain a precipitate of the sulphite of the metal, which you may filter off, wash, and dry, *e. g.*:—

$$BaCl_2 + K_2SO_3 = BaSO_3 + 2\,KCl.$$

Add hydric sulphate or chloride to any metallic sulphite; hydric sulphite will be formed, thus,

$$K_2SO_3 + H_2SO_4 = K_2SO_4 + H_2SO_3;$$

but H_2SO_3 very readily splits up into H_2O and SO_2, you therefore obtain sulphuric dioxide, which escapes in bubbles if there is not enough water present to hold it in solution. Most acid hydrogen salts are capable of effecting a similar decomposition of the sulphites, probably because SO_2 is so volatile. But a solution of sulphuric dioxide in water, which is at any rate potentially (in powers) equal to hydric sulphite, is capable of decomposing the carbonates and expelling carbonic dioxide, CO_2.

$$K_2CO_3 + H_2SO_3 = K_2SO_3 + H_2O + CO_2.$$

Precipitate some baric sulphite, and treat it with hydric chloride solution. It will dissolve.*

* For a reason which will appear shortly, you must use a sulphite which has been *very* recently prepared.

177. To the contents of a tube, in which zinc is dissolving in dilute hydric sulphate, add a small quantity of a sulphite, and hold over the mouth of the vessel paper moistened with solution of lead acetate. The blackening which occurs proves that sulphuretted hydrogen is formed :—

$$H_2SO_3 + H_6 = H_2S + 3\,H_2O,$$

i. e., the nascent hydrogen produced robs the hydric sulphite of its oxygen, and so *reduces* it to the state of hydric sulphide. This reaction constitutes a most excellent test for the presence of a sulphite. Hydric sulphite H_2SO_3 very readily takes up oxygen, and becomes H_2SO_4 (for proof see § 182).

178. Sulphuric trioxide or sulphuric acid (anhydrous) SO_3. This body is produced by the direct union of sulphuric dioxide with oxygen. This union will not take place at ordinary temperatures, or even at high ones, if there be not present some substance such as platinum to facilitate the combination.

Put some spongy platinum (or *clean* foil) into one end of a foot of narrow combustion tube, connect that end with the exit tube of a wash bottle containing oil of vitriol, and having oxygen passing into it by one tube and sulphuric dioxide by another. Gently heat the platinum as the mixed gases pass over it. They will unite, and thick white fumes of SO_3 will issue from the apparatus, or may even condense in the tube in the form of shining needles, if it (the tube) be surrounded at one part of its length by a mixture of ice and salt.

NOTE. Pass the gases slowly, and allow *two* bubbles of the sulphuric dioxide to pass through the washing bottle for each *one* of oxygen.

179. To an ounce of hydric sulphate (H_2SO_4) contained in a tubulated retort add an ounce and a half of phosphoric pentoxide (P_2O_5), and distil by a gentle heat into a small flask surrounded by ice and salt. Beautiful shining needles of sulphuric trioxide will condense, and should be sealed up by drawing off the neck of the flask before the blowpipe. The reaction which takes place may be represented thus,

$$H_2SO_4 + P_2O_5 = 2\,HPO_3 + SO_3,$$

i. e., the phosphoric pentoxide takes away the elements of one

molecule of water from hydric sulphate, leaving the so-called anhydrous sulphuric acid.

180. If sulphuric trioxide be thrown into water it combines with that body, with the evolution of so much heat as to produce a hissing noise, and again forms hydric sulphate. The two reactions last-mentioned, viz.,

$$H_2SO_4 - H_2O = SO_3 \text{ and}$$
$$SO_3 + H_2O = H_2SO_4,$$

lead us to regard hydric sulphate as a compound of the anhydrous (without water) body SO_3 with water.

181. There are other methods of preparing sulphuric trioxide which need not be introduced here. The properties of sulphuric trioxide are :—it is a white fibrous solid which melts at 25° C., giving a liquid which boils at 53° C. As before stated, it unites very violently with water, it also unites directly with many metallic oxides to form sulphates, *e. g.* :

$$SO_3 + PbO = PbOSO_3, \text{ or } PbSO_4.$$

It is found dissolved in hydric sulphate H_2SO_4, forming $\left.\begin{matrix} H_2SO_4 \\ SO_3 \end{matrix}\right\}$ or $H_2S_2O_7$, which is called Nordhausen oil of vitriol, or "fuming sulphuric acid," a body which is much used for dissolving the indigo which is to be used for dyeing. It is prepared at Nordhausen in Saxony, by distilling dried green vitriol, $FeSO_4$, at a red heat, in earthenware retorts; whence the name "oil of vitriol." If gently heated in a retort, it gives off the dissolved SO_3, which can be condensed in a well-cooled receiver. It fumes strongly in moist air, owing to escape of vapours of SO_3.

182. Hydric Sulphate, Hydrated Sulphuric Acid, Oil of Vitriol—

$$H_2SO_4 = 98 = 4 \text{ vol. or } \begin{array}{|c|c|} \hline 24{\cdot}5 & 24{\cdot}5 \\ \hline 24{\cdot}5 & 24{\cdot}5 \\ \hline \end{array}$$

can be obtained by acting on SO_3 by water, a process which is

impracticable on a large scale, or by oxidising hydric sulphite H_2SO_3, which is in effect the method always employed. A solution of sulphuric dioxide in water when exposed to the air slowly absorbs oxygen; or a mixture of SO_2, water vapour, and air will in the same manner become hydric sulphate.

These last statements can be proved by taking advantage of the fact that baric sulphate is insoluble in hydric chloride.

Expose some solution of sulphuric dioxide (hydric sulphite) in an uncorked bottle for a few days. Add to it baric chloride and diluted hydric chloride solution, a white precipitate of baric sulph*ate*, $BaSO_4$, will be formed. This precipitate cannot be baric sulph*ite*, because that body is *soluble* in the hydric chloride.

183. The oxidation of hydric sulphite by mere contact with air is too slow for manufacturing purposes; it is therefore found necessary to use some oxidising agent. The one employed is a gaseous oxide of nitrogen (N_2O_3), which readily gives up one-third of its oxygen to hydric sulphite, leaving thereby N_2O_2, which has the power of *quickly* uniting with the oxygen of the air to again form N_2O_3, which again gives up oxygen to another portion of hydric sulphite, and so on to an indefinite extent.

$H_2SO_3 + N_2O_3 = H_2SO_4 + N_2O_2$, and $N_2O_2 + O = N_2O_3$, which again reacts, as in the first equation, and so on *ad infinitum*.

184. In practice this reaction is employed thus:—Sulphur is burnt, or iron pyrites (FeS_2) is *roasted*, and the sulphuric dioxide formed is passed by a flue into a large leaden chamber, where it is mixed with steam blown in from other openings. This mixture, which is potentially hydric sulphite, is then oxidised by the action of nitric teroxide in small quantity, as explained in the last paragraph. A slow current of air is kept passing through the chamber by means of a chimney, so as to supply plenty of oxygen for the nitrous gas to transfer to the hydric sulphite. The hydric sulphate, as it is formed, collects in a layer of water placed on the bottom of the chamber, and is drawn off when the liquid so formed has attained a specific gravity of 1.5.

This liquid is used and sold under the name of "chamber acid," or "brown acid" (from its being coloured brown by a trace of organic matter); it consists of about 60 per cent. of pure hydric sulphate, H_2SO_4, and 40 per cent. of water. The water is removed by boiling the mixture. Water boils at 100° Centigrade; but hydric sulphate at 327° Centigrade. Accordingly, when such a mixture as above is heated, water first goes off, and when it has gone, and the temperature has risen to 327° Centigrade, the hydric sulphate goes too. The first part of the concentration is performed in leaden pans, which are not attacked to any great extent by diluted hydric sulphate; but when a certain point has been reached, it is necessary to use vessels of glass, or platinum, to finish the operation in. The account of the manufacture of "oil of vitriol" just given is a mere outline, and must not be supposed to represent with perfect accuracy a process, which is, in fact, much more complicated.

185. To represent in miniature, the preparation of this most important body, you may proceed thus :—

Arrange an apparatus like that shown in the figure, where (*a*) is a funnel having a little dish of sulphur below it, and connected by caoutchouc

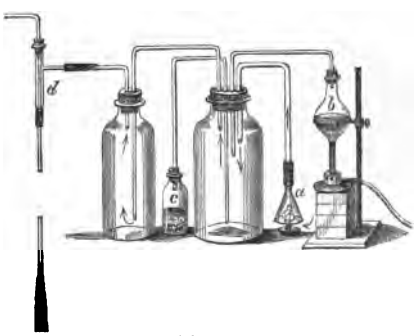


Fig. 49.

tube with a glass tube leading into the big bottle; (*b*) is a flask containing water to yield steam; (*c*) a small bottle containing copper turnings covered by dilute hydric nitrate, and (*d*) an aspirator, drawn on a larger scale on next page.

Light the sulphur, establish a current of air by turning on the water to the aspirator, boil the water in "*b*" and set *c* to work.

In the big bottle you will have a mixture of air, sulphuric dioxide, water vapour,* and nitric teroxide, produced by the union of the nitric dioxide made in *c* with the oxygen of the air. The changes before described will take place as the mixed gases pass on with the current, and both bottles will become filled with a reddish-tinted cloud of hydric sulphate and nitric teroxide. After having burnt about ½ oz. of sulphur, pour the liquid contents of the bottles out into a basin and evaporate cautiously till white irritating vapours begin to appear. Oil of vitriol will remain, and may be compared with a bought specimen.

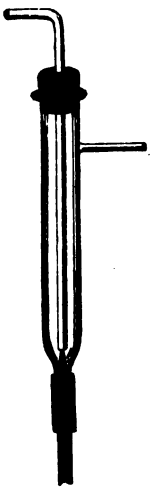


Fig. 50.

The construction and mode of action of the aspirator is this. The wide glass tube with the small right angle piece is six inches long, it is attached at its lower drawn-out extremity to a vertical tube of ¼ inch bore and as long as possible (40 feet is the *best*, but 4 feet will serve for the purpose of this experiment). The narrow tube which passes down the axis is drawn out to a point, and serves to convey a stream of water from a tap. As the water rushes down the long pipe it carries air with it, as big bubbles enclosed between small plugs of water. Therefore, any apparatus connected with the entrance tube will be deprived of a part of its air. If the tube is 40 feet long, a vacuum equal to that of a second-class air-pump is readily obtained. Quarter inch lead gas pipe is very suitable for the long tube, which can be passed through the wall of a room and down the outside of the house to a drain below.

186. Observe the following properties of hydric sulphate. It is, when pure, a colourless oily liquid, much heavier than water, as can be seen by pouring some slowly into a glass of water held between you and the light. (Its sp. gr. = 1.84.) It combines with water, evolving so much heat that it is dangerous to add water *to it*. If it is required to make a mixture of the two bodies, add it, little by little, to the water. It abstracts the elements of water from most organic substances, thereby charring them. Pour some over a lump of white sugar, drop some on

* Put also a small quantity of water at the bottom of each bottle.

wood, shake some up with oil—in each case the mass will turn black from liberation of carbon.

187. The density of the vapour of hydric sulphate, as determined by experiment, is only half that indicated by theory; that is, instead of being half its molecular weight (98) it is only one quarter. This apparent anomaly is explained by the fact, that when converted into vapour, it splits into H_2O and SO_3, each a complete molecule, occupying two volumes; it is therefore said to give a four volume vapour,

$$H_2SO_4 = \begin{array}{|c|}\hline SO_3 \\ \hline 40 \\ \hline 40 \\ \hline \end{array} + \begin{array}{|c|}\hline H_2O \\ \hline 9 \\ \hline 9 \\ \hline \end{array}$$

188. As mentioned and proved in §§ 122, 166, hydric sulphate, when hot, is a powerful oxidising agent. All common metals, except gold and platinum, are converted into sulphates by more or less prolonged boiling with the concentrated acid liquid, and many are dissolved by it, even when cold and dilute. These statements have already been proved in the course of preparing sulphuric dioxide and hydrogen.

189. Dilute a quantity of hydric sulphate with four or five times its bulk of water, and taste a portion of this after still greater dilution. It will be found intensely sour (don't swallow it).

Add a drop to a solution of blue litmus, a decoction of red cabbage, or tincture of violets; these blue or violet colours will be changed to red. Soak a little bruised turmeric root in methylated spirit, to which a drop or two of caustic potash has been added, and add to the deep brown liquid so obtained, a few drops of the diluted sulphate; the brown colour will become yellow.

190. Pour some into a solution of sodic carbonate (Na_2CO_3) or over powdered chalk ($CaCO_3$), a brisk effervescence will take place owing to the escape of carbonic dioxide (CO_2).

191. Add some slowly, and at last drop by drop, to a solution of caustic potash (KHO), a strongly alkaline body;* and test the well-stirred liquid with red litmus paper after each addition. A point will be reached at which the liquid has lost the power of turning the red paper blue, and yet

* See Ammonia.

has not acquired the power of turning blue litmus paper red; in other words, it will have become neutral or non-active as regards vegetable colours. At the same time it has lost its sour taste and its power of decomposing carbonates.

192. The properties exhibited by hydric sulphate in the above experiments; viz., sourness; power of changing vegetable blues red, and browns yellow; power of decomposing carbonates with liberation of carbonic dioxide, and especially the power of combining with, and more or less completely neutralising alkaline bodies, are those which are called *acid* properties.

All substances, possessing these powers, are said to be acid; *e. g.*, hydric chloride, hydric chlorate, sulphuric dioxide, &c., &c. Many bodies fail in one or more of these powers, yet, possessing the others, are rightly described as acid, *e. g.*, hydric sulphide will not decompose the carbonates of soda or potash, and is only capable of neutralising potash or soda to a very slight extent, and does not taste sour, nevertheless it is decidedly acid in character.

193. Those bodies which possess acid properties in a very high degree, and those which are in composition and other properties analogous to them, although exhibiting acid properties but faintly, are often, indeed generally, called "acids." This substantive use of the adjective "acid" is, however, objectionable, since some chemists apply it to those acid oxides, such as Cl_2O; Cl_2O_3; Cl_2O_5; SO_2; SO_3, &c.; and others to their hydrated derivatives, $HClO$; $HClO_2$; $HClO_3$; H_2SO_3; H_2SO_4, &c., which is productive of much confusion.

194. Neutralise some hydric chloride with soda, and evaporate off the water—salt (common salt) will be left. It is neutral, has a well-known salt taste, is crystalline and soluble. Dissolve it in water and add silver nitrate to it, its sodium becomes exchanged for silver.

$$NaCl + AgNO_3 = AgCl + NaNO_3.$$

The silver chloride is insoluble, consequently tasteless, and neutral. Wash the silver chloride, suspend it in water, and pass a stream of hydric sulphide—the silver will be replaced by hydrogen.

$$2AgCl + H_2S = 2HCl + Ag_2S.$$

The hydric chloride is soluble, and strongly acid.

195. Different as these three bodies, NaCl, AgCl, and HCl, are in their properties, they have this in common with the first (salt): they are composed of two dissimilar substances; one of them, chlorine, and the other an element with properties very opposite to those of chlorine. They, therefore, partake of the character of "salt," and are accordingly called salts. Hydric chloride is thus the hydrogen salt of chlorine; and the chlorides of the metals are the metallic salts of chlorine—H I, NaI, AgI are similarly salts of iodine, and iodine in them plays the part of chlorine in the chlorides, and is therefore called the "chlorous" element of these compounds.

The hydrogen, sodium, and silver are the "basylous" elements—"basylous" being understood to mean the opposite of "chlorous."

196. Evaporate the solution obtained by neutralising the hydric sulphate by potash and crystallise. You will obtain a *neutral* crystalline body, having the composition K_2SO_4, *i. e.*, of hydric sulphate, with all its hydrogen replaced by potassium. Divide another portion of hydric sulphate into two portions, neutralise one with potash and add the other—this is equivalent to neutralising half the original hydric sulphate—evaporate to dryness, and you will obtain a mass having the composition represented by $KHSO_4$, *i. e.* of hydric sulphate, with *half* its hydrogen replaced by potassium. This hydro-potassic sulphate is *strongly acid.* Dilute the residue contained in the flask used for preparing sulphuric dioxide, filter and crystallise. Cupric sulphate, $CuSO_4$, $5H_2O$, will be left as beautiful blue crystals, which have an acid reaction to litmus, notwithstanding that all the hydrogen of the hydric sulphate is replaced by the metal.

All salts which contain replaceable hydrogen are called acid salts, whether they have an acid reaction or not. When they have no replaceable hydrogen, they are said to be constitutionally neutral, even if they are physically acid, as in the case of $CuSO_4$, and most other soluble salts of the heavy metals.

H_2SO_4, K_2SO_4, $KHSO_4$, and $CuSO_4$, are salts consisting of "basylous," hydrogen, potassium, copper, and a group of elements, SO_4, which behaves as a chlorous divalent element.

197. If chemical language were perfectly consistent, all compounds of two dissimilar elements, or groups of elements, would

be called salts; but in practice the name salt is restricted to those bodies, which closely resemble, in properties or composition, or both, the typical salts named and described above. Observe, that of the above-mentioned salts, those which contain hydrogen are acid, and that the one which contains two atoms of hydrogen (H_2SO_4) is much more acid than the corresponding one ($KHSO_4$), which has only one atom left.

198. Because a molecule of hydric sulphate can have both its atoms of hydrogen replaced by equivalent quantities of metal, it is said to be dibasic.

199. Besides the sulphates described above, prepare sodic sulphate and hydrosodic sulphate from sodic hydrate:—ammonic sulphate and hydroammonic sulphate from solution of ammonia (*note*, in these cases use very dilute hydric sulphate, or you will have an explosive action) :—baric, calcic, and plumbic sulphates by precipitation. Write out the equation of each reaction you employ. As the sulphates are very important, and are of common occurrence, we will give a list of the chief ones with their formulæ, including water of crystallisation, and trivial names. Their systematic names are indicated by their formulæ:—

K_2SO_4		
$KHSO_4$	Sal enixum.	
Na_2SO_4, $10H_2O$	Glauber's salts.	
$NaHSO_4$		
$MgSO_4$, $7H_2O$	Epsom salts.	
$ZnSO_4$, $7H_2O$	White vitriol.	White copperas.
$FeSO_4$, $7H_2O$	Green vitriol.	Green copperas.
$CuSO_4$, $5H_2O$	Blue vitriol.	Blue copperas.

The above are soluble bodies which are easily crystallised.

$BaSO_4$	Heavy spar.	
$CaSO_4$, $2H_2O$	Selenite.	Alabaster, and (when dried), Plaster of Paris.
$PbSO_4$,		

Are insoluble, or nearly so, and are therefore only obtained in distinct crystals as minerals.

A trivalent metal, or a group which behaves like one, will

form a sulphate by replacing six atoms of hydrogen in three molecules of hydric sulphate, by two atoms of itself, *e. g.*,

$$(Al_2)^{vi} + 3H_2SO_4 = H_6 + (Al_2)^{vi}3SO_4,$$
$$(Fe_2)^{v}O_3 + 3H_2SO_4 = 3H_2O + (Fe_2)^{vi}3SO_4.$$

200. The presence of a soluble sulphate, even in minute quantity, is very easily detected by the use of baric chloride, or any other soluble barium salt, for baric sulphate is so very insoluble even in acid liquids, that the smallest quantity of it separates completely from a solution in the form of a white precipitate. By collecting the precipitate on a filter, washing, drying, igniting and weighing it, the weight of the sulphate present is found. $BaSO_4 = 137.5$, so for every 137.5 parts of it which is obtained, there must originally have been present such a quantity of the particular sulphate as contains one atom of sulphur.

E.g., 98 parts of H_2SO_4,
174 ,, K_2SO_4,
159·5 ,, $CuSO_4$.

Soluble lead salts also give a white precipitate in dilute solutions of the sulphates, if the liquid does not contain free fixed alkali or hydric chloride (in either of which lead sulphate is soluble).

201. Many sulphates, when heated to redness with carbon, lose all their oxygen, and thereby become reduced to sulphides.

Mix potassic sulphate (K_2SO_4) in fine powder, with half its weight of lampblack and a little oil or sugar;* ram the whole into an earthen crucible provided with a cover, and expose to a bright red heat for an hour. Allow the crucible to become *quite cold*, then break it and extract its contents, which will consist of potassic sulphide K_2S, a very useful reagent.

$$K_2SO_4 + C_4 = K_2S + 4CO.$$

Prove that the operation has been successful, by adding a little dilute hydric sulphate to a solution of a portion of the mass obtained.

$$K_2S + H_2SO_4 = K_2SO_4 + H_2S.$$

Other compounds of Sulphur with Oxygen and Hydrogen.

* To furnish finely divided carbon by its decomposition at a red heat.

202. If an alkaline sulphite be exposed to air, it slowly takes up oxygen and becomes a sulphate. But if instead of oxygen we expose it to sulphur, we get a new body. Thus, if we boil sodic sulphite with sulphur, we obtain the so-called hyposulphite of soda,

$$(Na_2SO_3)_2 + S_2 = 2\,Na_2SO_3S,$$

which is so largely used in photography for dissolving the iodide of silver which has not been altered by light. A better name for the salts corresponding to the one just mentioned is the thiosulphates, a name which indicates that they are to be considered as sulphates which contain sulphur in place of some of the oxygen. All the thiosulphates, when treated with hydric sulphate or chloride, are ultimately resolved into a chloride, or sulphate, of the metal, and sulphur and sulphuric dioxide from the decomposition of the hydric hyposulphite.

$$2\,H_2S_2O_3 = 2\,H_2O + 2\,SO_2 + S_2.$$

There are other compounds of sulphur and oxygen with hydrogen or metals: they have not been much studied and possess little interest.

They are four in number:

$H_2S_2O_6$	Hydric dithionate.
$H_2S_3O_6$	,, trithionate.
$H_2S_4O_6$	,, tetrathionate.
$H_2S_5O_6$	,, pentathionate.

Selenium and Tellurium.

203. Selenium = Se = 79.5; Tellurium = Te = 129; are two rare elements which closely resemble sulphur in their chemical relations, though in appearance they approach the metals. Selenium is a steel grey body, giving a red powder; it has a specific gravity of 4.5, and when crystallised conducts electricity slightly. Tellurium is a white brittle crystalline metal, which melts at about 500° C., has a specific gravity of 6.25, and conducts heat and electricity. Both elements burn in the air. They both form compounds with hydrogen, H_2Se and H_2Te, named respectively hydric selenide, or selenetted hydrogen, and hydric telluride, or telluretted hydrogen, which are obtained by methods similar to the one most used for preparing sulphuretted

hydrogen; viz., dissolving a metallic selenide, or telluride, in dilute hydric sulphate.

$$M_2Se + H_2SO_4 = H_2Se + M_2SO_4,$$
$$M_2Te + H_2SO_4 = H_2Te + M_2SO_4.$$

H_2Se and H_2Te are both foul smelling gases, which precipitate metallic solutions like sulphuretted hydrogen, and are decomposed by the oxygen of the air with deposition of selenium, or tellurium, as the case may be. Both elements form oxides analogous to sulphuric di- and trioxides, and these oxides, by addition of water, yield acid salts analogous to hydric sulphite and hydric sulphate. Thus—

SeO_2, selenic dioxide $+ H_2O = H_2SeO_3$, hydric selenite,
SeO_3, selenic trioxide $+ H_2O = H_2SeO_4$, hydric seleniate,
TeO_2, telluric dioxide $+ H_2O = H_2TeO_3$, hydric tellurite,
TeO_3, telluric trioxide $+ H_2O = H_2TeO_4$, hydric tellurate.

For further information on these rare bodies, larger works must be consulted.

QUESTIONS ON CHAPTER IX.

1. In what forms does sulphur occur in nature? How and from what is the sulphur of commerce obtained?

2. Describe the action of heat on sulphur. How is the plastic form of sulphur prepared, and how does it differ from the ordinary form?

3. How does sulphur resemble oxygen in its behaviour to hydrogen and the metals?

4. What is the composition of hydric sulphide by weight and by volume?

5. How is hydric sulphide prepared, and what are its properties?

6. Explain the action of air, chlorine, and sulphuric dioxide SO_2 on hydric sulphide.

7. What volume of oxygen is required to burn 1 litre of hydric sulphide?—*Ans.* 1·5 litres.

8. What volume of sulphuric dioxide will be formed?—*Ans.* 1 litre.

9. How much heavier than air is hydric sulphide?—*Ans.* 2·36 times nearly.

10. What volume of gas would result from completely decomposing

200 cubic centimetres of hydric sulphide by chlorine?—*Ans.* 400 cubic centimetres.

11. Give the formulæ of the oxides and sulphides of potassium, sodium, silver, calcium, zinc, bismuth, gold, and tin.

12. How much heavier than air, hydrogen, oxygen, and nitrogen, is sulphuric dioxide by calculation?

13. How can sulphuric dioxide be prepared from hydric sulphate.

14. What are the properties of sulphuric dioxide, and what is it used for?

15. How can sulphuric dioxide be obtained in a liquid form?

16. How can the union of sulphuric dioxide and oxygen be brought about?

17. What weight of hydric sulphate could be produced from 3·2 grammes of sulphur?—*Ans.* 9·8 grammes.

18. Describe in outline the manufacture of oil of vitriol.

19. What are the properties of hydric sulphate?

20. How is the presence of a sulphate in solutions detected?

21. How is the anomalous vapour density of hydric sulphate explained?

22. Give the systematic names of blue, green, and white vitriols, of Epsom Salts, and Plaster of Paris.

23. What properties do you include under the term "acid"?

24. How do hydrogen salts differ from metallic salts?

25. What do you mean by saying that hydric sulphate is dibasic?

26(*a*). If 10 cubic centimetres of sulphuretted hydrogen be decomposed by bromine, what volume of hydric bromide will be obtained? (*b*) What weight of sulphur will be separated?—*Ans.* 20 cc. of hydric bromide and ·01429 grammes sulphur.

27. Write in parallel lines corresponding compounds of oxygen and sulphur.

28. How can hydric sulph*ite* be converted into hydric sulph*ide*?

CHAPTER X.

204. ELEMENTS which unite with hydrogen in the proportion of one atom to three, and with chlorine in the proportion of one atom to either three or five, include;—

NITROGEN, PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH.*

Nitrogen itself has already been studied; we, therefore, now turn to its compounds.

205. AMMONIA $NH_3 = 17 = 2$ vol. | 8·5 | 8·5 |

is the only compound of nitrogen and hydrogen. Nitrogen, as before shown, is very inert, and we should therefore not expect it to unite directly with free hydrogen, and indeed it does not. Nascent elements, *i.e.*, those which are just being turned out of combination, and which we suppose have their *atoms* free and not combined into *molecules*, have far greater combining energy than those which have been in a separate state of existence for an appreciable time—a fact which receives a forcible illustration in the case now before us. If we cause by almost any means the two elements, nitrogen and hydrogen, to be evolved from other compounds, in presence of one another, they unite and form ammonia. In some cases it is not necessary that both elements be in the nascent state.

206. Before proceeding to prove and illustrate these statements, the student had better make himself acquainted with the

* Bismuth is not known to form any hydrogen compound.

following properties of ammonia, that he may be able to recognise it when formed.

With solution of ammonia of commerce observe

1st. Its smell both when strong and when much diluted; in the latter case notice that by heating the liquid the odour becomes stronger.

2nd. That the air above even a very dilute hot solution of ammonia possesses alkaline characters (turns moist turmeric paper brown, and red litmus paper blue (see also § 217)).

3rd. That if to a solution containing ammonia you add any acid body in excess, the properties above noted disappear.

4th. That by adding to an acidified solution of ammonia an excess of a strong alkali, such as potash (KHO) or lime (CaO), the ammonia is again liberated with its original properties.

207. When zinc or iron filings are moistened with water and exposed to the air, the hydrogen which is slowly liberated from the water unites with some of the nitrogen of the air, and ammonia in small quantities is formed. It can be detected by washing out the mass, after the lapse of a day or two, with pure distilled water, and testing the filtrate by Nessler's re-agent (§ 225).

208. Organic bodies, such as gelatine, albumen, fibrine, &c., which contain nitrogen, carbon, and hydrogen, give rise to the production of ammonia both on putrefaction and destructive distillation. In either case, as the bodies do not contain ammonia ready formed, we must suppose the two elements to unite on separation from their former combinations.

The pungent smell which is so evident in a stable which has been closed for some time is due to the presence of ammonia (as carbonate), produced by the alteration of "urea," CH_4N_2O.

Place a few fragments of glue, isinglass, horn, hair, cheese, dry flesh, or blood, or indeed any animal matter, except fat, in a test-tube fitted with a cork and delivery tube passing to the bottom of a second test-tube containing a small quantity of water. Heat the material strongly by a lamp while the tube containing it is held nearly horizontal, and continue the operation as long as anything distils over. A black mass remains in the first tube, while the second contains a variety of watery and oily liquids of especially foul smell. The watery part will be found to contain much ammonia.

209. The process just described is called *destructive* distillation, because the whole of the original matter is destroyed, and new compounds, not originally contained in it, are obtained in the portion distilled. It is destructive distillation of nitrogenised organic bodies which furnishes the prime source of all the ammonia of commerce. At one time horn, and especially the horn of the "hart," was thought to be the best material for preparing ammonia. The solution of ammonia in water is still known as spirits of hartshorn. At present the gas-works furnish all the ammonia we employ. The watery liquid which collects along with the tar, when neutralised with an acid hydrogen salt, *e.g.* H Cl, yields a salt of ammonia, which, after purification, may be used for the preparation of pure ammonia.

210. When the oxidised compounds of nitrogen are submitted to the action of nascent hydrogen, their oxygen is removed in the form of water, and hydrogen takes its place in such proportions that ammonia results.

To the contents of a test-tube in which hydrogen is being evolved by the action of zinc on dilute hydric sulphate, add a small quantity of any nitrate or nitrite. The effervescence will perceptibly diminish in violence, owing, of course, to the fact that some of the hydrogen is oxidised before it can assume the free condition. Supposing we used hydric nitrate HNO_3, the reducing action would be represented by the equation

$$HNO_3 + H_8 = 3H_2O + NH_3,$$

but as the liquid is acid no smell of ammonia will be perceived. Boil it with soda or potash, and you will obtain abundant evidence of the presence of ammonia.

Heat a mixture of zinc and iron filings with a strong solution of potash, hydrogen will be evolved (see § 42). Add a solution of saltpetre (potassic nitrate KNO_3), ammonia will be rapidly given off. By this method the whole of any given quantity of nitrogen contained in a solution in the form of a nitrate can be converted into ammonia. Compare these reactions with that of nascent hydrogen on hydric sulphite, § 177.

211. Sal-ammoniac, or ammonic chloride, is a salt produced by the neutralisation of the ammoniacal gas liquors by hydric chloride, and purification by sublimation, its formula = NH_3HCl. To procure ammonia from it, it is only necessary to take away the hydric chloride; this can be done by the use of any strong alkali.

Commercial sal-ammoniac is to be coarsely powdered and introduced into a flask, together with its own weight of slaked lime or caustic soda in small lumps, and enough water to make the whole into a thick mud. On the application of heat, ammonia in the form of a colourless gas will be given off, and may be collected either over mercury or by upward displacement.

The reactions in the two cases being

$$\underbrace{Ca\,O}_{\text{Lime,}} + 2\,N\,H_3\,H\,Cl = Ca\,Cl_2 + H_2O + 2\,N\,H_3$$

$$\underbrace{Na\,H\,O}_{\text{Soda,}} + N\,H_3\,H\,Cl = Na\,Cl + H_2O + N\,H_3,$$

in each the metal of the alkali takes the chlorine of the ammonic salt, and its oxygen takes the hydrogen of the hydric chloride. Each molecule of ammonic chloride yields one of ammonia, *i.e.* 53·5 parts (grammes, tons, &c.) of ammonic chloride give 17 parts of ammonia.

The gas should be passed through a cold empty bottle to free it from the greater part of the water vapour, and the whole of

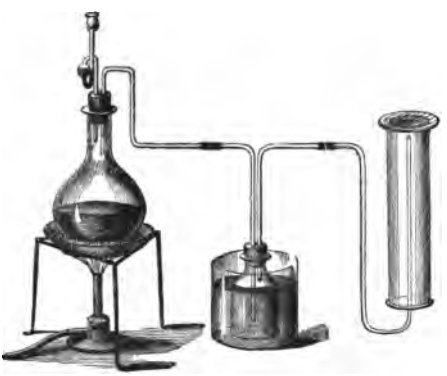


Fig. 51.

the spray which comes over with it (Fig. 51). If the gas is wanted in a dry state, it must be passed through a tube containing lumps of *solid potash*, not through calcic chloride, which absorbs it, or through oil of vitriol, which combines with it with explosive violence.

212. The composition of ammonia by volume may be shown by passing a long series of electric sparks through a known volume

of the gas contained in a eudiometer (such as that shown in fig. 29) standing over mercury. A small Ruhmkorf's coil worked by two or three cells of a good battery will be needed for this experiment. As the sparks pass, the gas gradually decomposes into its constituents, and its volume continues to increase until it has reached twice its original bulk. If oxygen, about equal in volume to the ammonia used, be now admitted, and exploded with the hydrogen liberated, the contraction which will take place will show that the *decomposed* ammonia contained three volumes of hydrogen to one of nitrogen,* or, to give substance to this, we will take a case :—

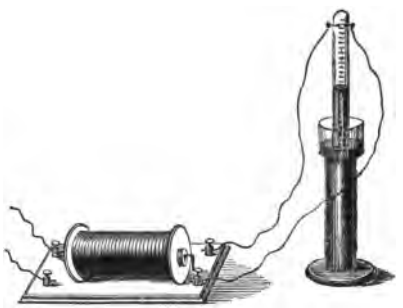


Fig. 52.

Vol. of ammonia introduced into the eudiometer . . . . . = say 16 cubic centim.
After passage of a long series of sparks through the gas it becomes . . = 32 „
Add oxygen to contents of tube, and say the total gas now . . . . = 50 „
It is evident that 18 cubic cent. of oxygen have been added.
Again pass an electric spark, and after explosion again measure the gas, it will be found that the 50 cubic cent. of mixed nitrogen, hydrogen, and oxygen have been reduced to . . 14 cubic centim.

Now 50 — 14 = 36, that is, the explosion has caused a loss of volume of 36 cubic cent. But this loss is due to the for-

* The precautions mentioned in § 30 must be attended to.

mation of water, which has condensed into an inappreciable bulk; and as we know that water contains two volumes of hydrogen for one volume of oxygen, we know that $\frac{2}{3}$ of this loss of 36 cubic cent. must be due to the hydrogen given by the decomposed ammonia, $\frac{2}{3} \times 36 = 24$. That is, in the 32 measures of the product of the decomposition of ammonia there are 24 measures of hydrogen, and therefore 8 of nitrogen. But as these volumes were contained in the original 16 measures, it is shown that that ammonia contained 8 measures (half its volume) of nitrogen, and 24 measures ($1\frac{1}{2}$ times its volume) of hydrogen, condensed into 16 measures, or one volume, which may be thus represented :—

$$\boxed{N=14} + \boxed{H=1} + \boxed{H=1} + \boxed{H=1} = \boxed{\frac{NH_3 = 8{\cdot}5}{2}} \boxed{\frac{NH_3 = 8{\cdot}5}{2}}$$

As nitrogen is 14 times as heavy as hydrogen, bulk for bulk, this experiment also shows that every gramme of hydrogen is united with $4\frac{2}{3}$ grammes of nitrogen ($\frac{1}{3}$ = $4\frac{2}{3}$).

213. If potassium be heated in dry ammonia gas, an olive green body, of the composition NH_2K is formed, *i.e.*, ammonia in which one-third of the hydrogen is replaced by potassium. If we knew nothing about the composition of ammonia by volume, the existence of this substance (potassamide) would be sufficient to show that ammonia contains three atoms of hydrogen, and that consequently it cannot be represented by NH, in which $N = 4\frac{2}{3}$ (compare with proof of composition of water § 56), but must have a formula of NH_3, in which $N = 14$.

214. We may represent the composition of ammonia by weight and by volume by a diagram, the form of which is strongly recommended for adoption when any problem relating to gas volumes has to be solved :—

$$\begin{aligned} N &= 14 = 1 \text{ vol.} \\ H_3 &= 3 = 3 \text{ vol.} \\ \hline NH_3 &= 17 = 2 \text{ vol.} \therefore 1 \text{ vol.} = 8{\cdot}5. \end{aligned}$$

This exhibits at a glance the facts that ammonia is only 8·5 times as heavy as hydrogen, that its constituents, if free, would occupy twice its own bulk, and that the hydrogen alone contained in any quantity of it would fill 1½ times as great a space as the ammonia it was derived from.

215. Ammonia, obtained as directed, is a colourless gas, having a peculiar, very irritating, but not disagreeable smell; of specific gravity 0·5967, as determined by experiment, at 15° C.; it is condensible to a liquid form by cooling to − 40° C. at the ordinary atmospheric pressure, or by a pressure of about 7 atmospheres at ordinary temperatures. The liquid ammonia can be solidified by extreme cold to a transparent solid. Its condensation by pressure may be performed by exposing dry silver chloride to dry ammonia gas till it absorbs no more, and then heating the body so obtained to 120° C. in one limb of a strong, sealed, **A**-shaped tube, the other end of which is kept in a mixture of ice and salt. The ammonia is expelled from its state of combination by the heat, and as it accumulates in the tube exerts a constantly increasing pressure on its own particles, till the point is reached at which it begins to condense, when it collects in the cold extremity.

Fig. 53.

216. Ammonia gas is as much lighter than air as $\frac{8{\cdot}5}{14{\cdot}4}$, and can be poured upwards through air, as shown in fig. 54. The transference of the gas from one jar to the other can be

shown by placing the mouths of both below water, which will rise into the one containing the ammonia. It does not burn in cold air, but does so in pure oxygen, forming water, and leaving nitrogen free,

$$4\,NH_3 + 3\,O_2 = 2\,N_2 + 6\,H_2O.$$

If a mixture of ammonia and oxygen be passed over spongy platinum, both the elements of ammonia will unite with oxygen and water, and hydric nitrate will result. Ammonia is resolved into its elements (slowly and imperfectly) by passage through a red-hot tube; it consequently acts as a reducing agent when passed over heated metallic oxides. Water, at ordinary temperatures, dissolves more than seven hundred times its volume of the gas with enormous rapidity. Try this as in the case of hydrochloric acid gas, taking care to hold the bottle firmly. Pass ammonia gas, which has traversed a cold empty wash-bottle, into a measured quantity of water, in a narrow glass, until no more is absorbed. Observe the suddenness with which the bubbles condense, the rise of temperature, and the increase of volume (amounting to nearly a third) which takes place. Take the specific gravity of the liquid; you will find it less than that of water.

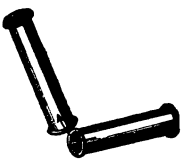


Fig. 54.

The solution so obtained is the "ammonia," "liquid ammonia," or "spirits of hartshorn" of commerce, which has the well-known pungent smell of ammonia gas itself, which needs no description. When boiled, the solution gives off its ammonia, and thus furnishes a ready means of preparing the gas when wanted for the purposes of experiment. The apparatus employed is that shown in fig. 38, on p. 67, only the gas is collected by upward displacement.

217. The often-used term "alkaline" is employed to designate the possession of those properties which ammonia or potash exhibit in the following experiments:—

Dilute some solution of ammonia, and some of potash; and with each—

Observe the taste, which will be found peculiar, and resembling that of soap or washing soda, but not either sour, salt, or bitter:—

Their action on various vegetable colouring matters will be found to be the exact opposite of that exerted by acid bodies, *e.g.*, they turn red litmus blue, red cabbage solution green, yellow turmeric paper brown.

When brought in contact with carbonic dioxide gas they absorb and combine with it (for mode of performing this experiment, see Carbonic Dioxide). When gradually added to an acid liquid they destroy its acid characters, as shown in the experiment detailed in connection with hydric sulphate.

Those bodies which are most highly alkaline are called alkalies. Potash, K H O, soda, Na H O, and ammonia solution, $N H_3 H_2 O$, are those which are meant by "the alkalies." Lime, Ca O, and baryta, Ba O, are called alkaline earths. Ammonia is called the volatile alkali; the others are called "fixed," because they are not dissipated by heat.

No body is capable of exhibiting all the alkaline powers, unless it is capable of existing in solution in some liquid of neutral character, but many exhibit the most important and distinctive one, viz., that of more or less completely neutralising acid bodies, even if quite insoluble in all liquids which do not chemically alter them. Such are the lower oxides and hydrates of most metals, *e.g.*, $Ag_2 O$, Cu O, Pb O, Zn O, &c., and $Cu (H O)_2$, $Pb (H O)_2$, &c., which are so lightly soluble in water that they hardly affect test papers; but, nevertheless, when added in sufficient quantity to strongly acid bodies, combine with and in a great degree neutralise them—forming metallic "salts" in so doing. This power of combining with and neutralising "acids" is termed basic power, and the bodies which possess it are called basic bodies, or for shortness, "bases." Alkalies may, therefore, be defined as soluble bases.

218. The most important property of ammonia is exhibited by the following experiment:—

Take two equal sized wide-mouthed bottles with broad lips ground flat with emery and turpentine on a slate; fill one with dry hydric chloride, the other with dry ammonia. Grease the lip of each and press them

together. Immediately dense white fumes begin to form, and in a short time both bottles will be coated internally with a snowy white powder. After action has ceased separate the two bottles, and notice the air rushes in to supply the vacuum caused by the condensation of both gases to the solid condition.

Fig. 55.

$$NH_3 + HCl = NH_3HCl.$$

If exactly equal volumes (for $NH_3 = 2$ vol., and $HCl = 2$ vol.) of each gas were employed, the body formed would be neither acid nor alkaline; but as an excess of one is, in practice, always present, the mass, when dissolved, is never quite neutral. This is one of the few instances of direct union of complete molecules.

219. Ammonia unites with other hydrogen salts (hydrated acids) in the same direct manner that it does with hydric chloride. If the hydrogen salt contains more than one atom of replaceable hydrogen, *e. g.*, hydric sulphate, H_2SO_4, then as many molecules of ammonia can combine with it as there are atoms of such replaceable hydrogen; but it can also form a definite compound by taking up only one molecule of ammonia.

Neutralise with ammonia an ounce or so of hydric nitrate, sulphate, and chloride in separate vessels, and crystallise the salts obtained. Their solutions will be neutral. (N.B. Dilute the acid hydrogen salts well before adding the ammonia, or you will have an accident.)

220. The compounds of ammonia with hydrogen salts are known under the name ammoniacal salts, or ammonic salts. They so closely resemble the corresponding potassic salts, both in form and general chemical characters, that they are supposed, like them, to contain a metal. Now the composition of potassic sulphate, nitrate, or chloride, for example, is represented by the following formulæ:—K_2SO_4; KNO_3, and KCl, while the *ammonic* sulphate, nitrate, or chloride, being built up by the addition of two molecules, or one of ammonia (NH_3), to the hydrogen salts, will have formulæ—

$$\left.\begin{matrix} NH_3 \\ NH_3 \end{matrix}\right\} H_2SO_4 \qquad NH_3HNO_3 \qquad NH_3HCl.$$

If we put these two sets of formulæ side by side, and endeavour to give them comparable forms, we see that we can do so by adding the hydrogen of the hydrogen salts, in the ammoniacal salts, to the ammonia, and so creating a group (NH_4), which may be looked on as playing the part of potassium in the other set. Thus—

NH_3	HCl	becomes	$(NH_4)Cl$	analogous to	KCl.
NH_3	HNO_3	,,	$(NH_4)NO_3$	,,	KNO_3
$(NH_3)_2$	H_2SO_4	,,	$(NH_4)_2SO_4$	,,	K_2SO_4.

This group (NH_4), which plays the part of a monovalent metal, is called ammonium. Its existence is hypothetical only; it has never been obtained in the free state. It is, however, very convenient, in considering many, or rather most, of the reactions of ammonic salts, to admit the "ammonium theory;" but it must not be forgotten that it is a theory.

221. The following reactions almost force on us a belief in the existence of ammonium:—

When potassic chloride is submitted to electrolysis, a globule of mercury being the negative pole, potassium is liberated from its state of combination, and dissolves in the mercury with formation of a semiliquid amalgam.* Ammonic chloride, similarly treated, gives an amalgam also.

Both amalgams, when thrown into water, give rise to the liberation of hydrogen, and leave alkaline solutions. The action of potassium on water is well known; it is ($K_2 + 2H_2O = H_2 + 2KHO$). Now if ammonium, NH_4, be contained in the ammonium amalgam, the reaction must be $(NH_4)_2 + 2H_2O = H_2 + 2NH_4HO)_2$, and as KHO, potassic hydrate, is powerfully alkaline, so should be NH_4HO, ammonic hydrate.

Note.—The method of performing the above experiments is not given, since a knowledge of voltaic electricity cannot be

* *Amalgam* is a name given to the solutions of other metals in mercury, with formation of compounds which retain the metallic lustre. With the exception of ammonium (if it be an exception) only metals are known to form such compounds.

assumed. A full description of a very simple method, and apparatus for the purpose, will be found in Golding Bird's "Elements of Natural Philosophy," p. 372.

Ammonium amalgam may be prepared by another and simpler process, which the student can readily carry out. Prepare about four ounces of a saturated solution of ammonic chloride in a basin. Then make a little sodium amalgam by throwing a bit of sodium the size of a large pea on to the surface of a quarter of an ounce of wet mercury in a test-tube (the two metals unite with a slight flash). Immediately pour the sodium amalgam into the ammonic chloride. A rapid action at once commences; the mercury swells up to one or two hundred times its former bulk, but retains in a great measure its lustre. The swollen mass when removed from the liquid and exposed to the air or thrown into water decomposes in a short time *with evolution of hydrogen and ammonia*.

The action, which doubtless takes place, is an interchange of sodium and ammonium, the first quitting the mercury to combine with chlorine, which the ammonium leaves for the mercury.

$$N H_4 Cl + Na Hg_n = N H_4 Hg_n + Na Cl.$$

Hg_n means that it is an unknown multiple of the atomic weight of mercury which takes part in this reaction.

222. When ammonia gas is passed into water, it is supposed to form ammonic hydrate, $N H_4 (HO)$, corresponding to potassic hydrate, $K (H O)$, for in a majority of cases the two bodies behave alike, *e. g.*: To two portions of ferric chloride add potash and ammonia respectively. In each will be obtained a precipitate of ferric hydrate: thus—

$$Fe_2 Cl_6 + 6 K (H O) = Fe_2 (H O)_6 + 6 K Cl$$
$$Fe_2 Cl_6 + 6 N H_4 (H O) = Fe_2 (H O)_6 + 6 (N H_4) Cl.$$

i. e., potassic and ammonic hydrates in reacting with ferric chloride, produce ferric hydrate and $\left\{\begin{matrix}\text{ammonic}\\\text{potassic}\end{matrix}\right\}$ chloride. These two bodies (potash and ammonia solutions) react similarly with zinc salts, *e. g.*, the sulphate, $Zn SO_4$, giving first a precipitate of zinc hydrate (which carries down a little zinc sulphate

with it), and then re-dissolving that precipitate when added in excess.

Other metallic solutions may be substituted for the ferric and zinc salts; but as ammonic and potassic hydrates are analogous only, and not identical, the reactions will, to the unpractised operator, sometimes appear very different, as ammonia often dissolves the precipitates first formed by it.

Ammonic hydrate has not been obtained in a separate state; its existence is therefore only hypothetical.

223. Though ammonia forms such unstable compounds with water, it combines readily enough with its analogue H_2S, which is indeed weakly acid—

$$\left.\begin{matrix}NH_3 + H\\ H\end{matrix}\right\}S = \left.\begin{matrix}NH_4\\ H\end{matrix}\right\}S, \text{ and } \left.\begin{matrix}NH_3\\ NH_3\end{matrix}\right\} + \left.\begin{matrix}H\\ H\end{matrix}\right\}S = \left.\begin{matrix}NH_4\\ NH_4\end{matrix}\right\}S.$$

The first ammonic sulphydrate and the second ammonic sulphide. Ammonic sulphydrate is a moderately stable crystallisable body produced by mixing equal volumes of hydric sulphide and ammonia gas, and which behaves towards metallic solutions in a manner which is almost identical with the reactions of the potassic or sodic sulphydrate, *e. g.*—

$$Mn\,Cl_2 + 2\,K\,H\,S = Mn\,S + H_2S + 2\,K\,Cl,$$
$$Mn\,Cl_2 + 2\,(NH_4)\,H\,S = Mn\,S + H_2S + 2\,(N\,H_4)\,Cl.$$

224. Some of the principal ammoniacal salts are here given. With the exception of the carbonates and sulphides they are devoid of all smell of ammonia. Those in which ammonium *fully* replaces the hydrogen of the hydrogen salt are mostly neutral, never acid.

$(NH_4)\,Cl$	ammonic chloride. Sal-ammoniac	(neutral).
$(NH_4)\,NO_3$	,, nitrate.	(neutral).
$(NH_4)\,ClO_3$	,, chlorate.	(neutral).
$(NH_4)\,HSO_4$	hydro-ammonic sulphate	(acid in reaction).
$(NH_4)_2\,SO_4$	(di)ammonic sulphate	(neutral).
$(NH_4)\,HSO_3$	hydro-ammonic sulphite	(acid).
$(NH_4)_2\,SO_3$	(di)ammonic sulphite	(neutral).

$(NH_4)HCO_3$ hydro-ammonic carbonate (alkaline in reaction).
$(NH_4)HC_2O_4$ hydro-ammonic oxalate (acid).
$(NH_4)_2C_2O_4$ (di)ammonic oxalate (neutral).
$(NH_4)(CN)$ ammonic cyanide (alkaline).

225. The tests for ammonia are those given in § 206, and "Nessler's test," which is employed to detect very minute traces of ammonia, such as occur in rain water.

A solution of potassic iodide is to be added gradually to a solution of mercuric chloride, $HgCl_2$, till precipitation ceases,

$$HgCl_2 + 2KI = 2KCl + HgI_2,$$

then the addition of the potassic iodide continued till the scarlet precipitate is nearly but not quite dissolved, the liquid filtered, rendered *strongly alkaline* with potash set aside to settle; and the clear liquid decanted for use.

This liquid when added to water containing even ·0000001 of its weight of ammonia, gives a distinct brown coloration at once, and after a time a precipitate, having the composition $I_2N_2Hg_4$, and called iodide of tetra-mercur-ammonium.

To detect ammonia by the use of this re-agent, when any of the metals other than potassium and sodium are present, it is necessary first to distil the suspected liquid with an excess of potash or lime, and to apply the test to the distillate.

226. Tetrachloride of platinum, $PtCl_4$, when added to a solution of ammonic chloride combines with it to form a double salt (which precipitates as a bright yellow crystalline powder), which is very slightly soluble in water, and still more slightly in alcohol. This salt, which has the composition $(NH_4Cl)_2PtCl_4$, or $Pt(NH_4)_2Cl_6$, is so insoluble in alcohol, and so stable, that it is possible to collect it on a filter, wash it with alcohol, and dry it without sensible loss. From its weight may be calculated the quantity of ammonia in the original liquid to which the platinic chloride was added. As further illustrating the similarity of ammonium and potassium compounds, observe that when platinic chloride is added to a solution of potassic chloride, a precipitate having in all respects the same appearance as the ammonic compound is formed. Its composition is $(KCl)_2PtCl_4$. Both compounds, when ignited, are decomposed; metallic platinum in the spongy form being left; pure when the ammonium salt is used, mixed with potassic chloride in the other case.

Note.—All the salts of ammonia not containing a true metal or a non-volatile acid, such as phosphoric, are dissipated by a red heat, and all without exception lose the whole of their ammonia when ignited.

227. Nitrogen is an essential constituent of most animal bodies, and of many parts of all plants, but neither plants nor animals can assimilate *free* nitrogen. Animals obtain their nitrogen directly or indirectly from plants, which obtain theirs from the *compounds* of nitrogen existing in the soil, air, and water with which they are supplied. If crops are continually removed from the same portion of land and nothing returned, the soil becomes barren; but if the land be duly manured an unlimited succession of crops may be taken. The manure returns to the soil those ingredients which are removed with the plants. Among the bodies so returned combined nitrogen is one of the most important. Those manures containing the most nitrogen are, therefore, other things being the same, the most efficacious. Guano, which is the dry excrement of sea birds, contains a large quantity of ammoniacal salts; stable-dung when duly rotted also contains much ammonia. In ammonia the nitrogen is in a form very readily assimilated by plants, therefore, these two things constitute very effective and stimulating manures.

The presence of nitrogen in an organic body can best be shown by igniting the body with solid potash in a test tube; when all the nitrogen will be evolved in the form of ammonia.

Chloride and Iodide of Nitrogen (?).

228**. Nitrogen is said to form a chloride of the composition $N Cl_3$, but it is not certain that the body has the composition assigned to it, since it is so explosive that it is almost impossible to purify it sufficiently for an accurate analysis. It is prepared by filling an absolutely clean bottle with chlorine, and then standing the mouth downwards in a perfectly clean saucer of lead containing a strong solution of ammonic chloride. Yellow oily drops collect after a time, and consist of the body in question. The bottle must be removed cautiously, and the drops exploded by touching them with the greasy end of a very long stick. It is an experiment far too dangerous to be attempted by any but a very good operator, since the explosion may occur before it is wished, if there is the least trace of dirt

about any part of the apparatus, and when it does occur it blows everything near into bits.

An analogous compound of nitrogen with iodine (and probably hydrogen) may be prepared with more safety in small quantity. Throw a grain or two of powdered iodine into a small glass of very strong solution of ammonia. After the lapse of half an hour pour off the liquid from the black sediment, and distribute the latter over a number of bits of blotting paper, which set aside to dry in the air. When quite dry, it will be only necessary to touch the spots of iodide of nitrogen with a feather, or even simply to move the paper on which they rest, in order to produce a sharp explosion.

QUESTIONS ON CHAPTER X.

1. What is the composition of ammonia? Give its formula.

2. What is the chief source of the ammonia of commerce?

3. (*a*) How is ammonia gas prepared? (*b*) Give the reaction in symbols. (*c*) Describe the properties of the gas. (*d*) How much nitrogen is there in 100 grains of it?—*Ans.* $82 \cdot \frac{6}{17}$ grains.

4. (*a*) How much ammonic chloride must I use in order to get 100 grammes of ammonia? (*b*) How many cubic centimetres of hydrogen will that ammonia contain?—*Ans.* (*a*) 314·7 grammes NH_4Cl. (*b*) 197647 cubic centimetres H.

5. What is the capacity of a vessel which will hold 83 grammes of ammonia at 0° C., 30 in. bar. press.?—*Ans.* 109·4 litres, nearly.

6. (*a*) If 29 cubic centimetres of ammonia gas be completely decomposed by a series of electric sparks, what volume of gas will be obtained?—*Ans.* 58 cubic centimetres.

(*b*) If the product of the decomposition be mixed with 30 cubic centimetres of oxygen and the mixture exploded, what will be the volume of the residue, and what *gases* will it consist of? *Ans.*

$$\left\{\begin{array}{l} 14 \cdot 5 \text{ cu. c. N} \\ \underline{8 \cdot 25 \text{ cu. c. O}} \\ 22 \cdot 75 \text{ total volume remaining.} \end{array}\right.$$

7. What weight of ammonia could be obtained from 267·5 grammes of sal-ammoniac?—*Ans.* 85 grammes.

8. What weight of ammonia gas would be required to neutralise 4·9 grammes of hydric sulphate?—*Ans.* 1·7 grammes.

9. What is the ammonium theory?

10. What evidence is there in favour of classing ammonium among the metals?

11. Apart from its composition by volume, what proof is there that ammonia contains *three* atoms of hydrogen?

12. Why is guano useful as a manure?

13. Give the formulæ of ammonic and hydro-ammonic sulphates; of ammonic hydrate, oxide, sulphide, and sulphydrate.

14. By what method would you seek for proof of the presence of minute traces of ammonia in a liquid?

15. Give the tests generally used to detect the presence of ammonia.

16. What do you mean when you say that ammonia is alkaline, or that it is an alkali?

17. To what body would you compare the solution of ammonia, and why do you consider the two to be analogous?

18. Under what conditions do nitrogen and hydrogen unite?

19. How may nitrogen in organic bodies be detected?

20. How may ammonia be obtained from the compounds of nitrogen and oxygen?

21. Explain why the reagents ordinarily used to dry gases cannot be used for drying ammonia.

22. What is an amalgam?

23. Compare ammonium with potassium.

24. What are basic oxides?

CHAPTER XI.

OXIDISED COMPOUNDS OF NITROGEN.

229. WHEN nitrogenised organic bodies decay in presence of alkalies, or alkaline earths, as when dung is allowed to rot in contact with lime or wood ashes, their nitrogen is found not to take the form of ammonia, but to remain in combination with the metal of the alkali and a considerable quantity of oxygen, in the shape of nitrates; MNO_3, or M''_2NO_3.

In many parts of India there are natural beds of nitre, or potassic nitrate, KNO_3, occurring, for the most part, in places which have at one time been thickly inhabited, and where, consequently (in the total absence of drains), the animal refuse of all kinds has become mixed with the ashes of wood used as fuel, and has there rotted in contact with the alkaline carbonate of potash contained in those ashes. Sodic nitrate, $NaNO_3$, occurs in enormous masses in Chili and Peru; its origin is unknown.

230. *Hydric Nitrate*—Nitric acid—$HNO_3 = 63$—is readily obtained from either potassic or sodic nitrate, by replacing the metal by hydrogen by means of the usual reaction with hydric sulphate.

Put a pound of saltpetre (potassic nitrate) into a non-tubulated retort, of such a size that it is only one-third filled with it. Weigh out a quantity of strong oil of vitriol sufficient to re-act on the nitrate according to the equation

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3,$$

and pour it on to the salt by means of a funnel tube long enough to reach the bulb. Support the retort on a stand with its neck slanting upwards, and apply a gentle heat. Red fumes will appear, and a liquid will condense in the neck and run back into the body of the retort and carry with

it the grains of potassic nitrate, &c., which adhere to the sides. When the neck of the retort is washed clean in this way, turn it down and arrange the apparatus shown in fig. 55 (and explained under Apparatus). Continue to distil at a moderate temperature till liquid ceases to drip from the neck of the retort, and the contents of the body are in a state of tranquil fusion.

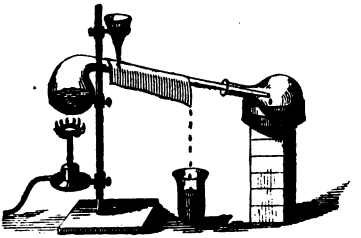


Fig. 55.

Red fumes will appear at the beginning and end of the operation—they consist, not of the vapour of hydric nitrate, but of the products of its decomposition by heat. They are soluble in hydric nitrate, and consequently, the liquid obtained by the operation described is of a deep yellow colour. Warm the contents of the receiver flask for some time, the liquid will become colourless owing to the expulsion of the dissolved red gas (N_2O_4). At the same time, any hydric chloride derived from common salt in the nitre will be expelled.

231. The hydro-potassic sulphate $HKSO_4$ formed in the reaction indicated above, is capable of reacting on potassic nitrate so as to replace its potassium by hydrogen,

$$HKSO_4 + KNO_3 = K_2SO_4 + HNO_3,$$

just as hydrosodic sulphate acts with sodic chloride, but just as in that case it requires a high temperature, and consequently, much decomposition occurs. We may, therefore, use only half the quantity of hydric sulphate indicated above, if we distil at a high enough temperature.

$$H_2SO_4 + 2KNO_3 = K_2SO_4 + 2HNO_3.$$

On a manufacturing scale, sodic nitrate, or Chili saltpetre as it is called, is heated with a quantity of hydric sulphate, such as to furnish (di)sodic sulphate.

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3.$$

232. The hydric nitrate, finally obtained by the above process, is a colourless liquid which fumes very strongly in moist air, has a density of 1·52, and boils at 84° C. (partially decomposing at the same time into oxygen, water, and nitric peroxide, N_2O_4). It decomposes somewhat by exposure to light into oxygen, nitric peroxide, N_2O_4, and water.

1st. Try its sour taste, and acid reaction, after diluting with 20 parts of water.

2nd. Action on skin and animal matter generally; tried with a finger, and some white wool, both of which will turn yellow (the fuming nitrate, diluted with its own bulk of water, is to be used).

233. Boil together gently some of the strongest hydric nitrate and flowers of sulphur in a test tube; after a time the sulphur will dissolve; dilute with water, filter, and test for the presence of a sulphate (§ 200). As the sulphur has been converted into hydric sulphate, the hydric nitrate must have given it oxygen. Again, as seen before (§ 128), iodine is converted into hydric iodate by boiling with hydric nitrate.

These and numberless other experiments convince us that hydric nitrate is a powerful oxidising agent. One very good experiment, to illustrate this most important property of the body, is to pass bubbles of sulphuretted hydrogen into it while gently heated. If the nitrate be sufficiently strong both the hydrogen and sulphur will be oxidised.

234. Metallic tin and antimony, when thrown into somewhat dilute hydric nitrate, are converted into oxides, which appear in the form of yellowish white powders, and at the same time dense red fumes of low oxides of nitrogen are given off. Gold, platinum, and aluminium alone, among the common metals, resist its action; all the others are either dissolved by it as nitrates, or converted into oxides.

235. The metallic nitrates are formed by solution of the metal, or its oxide, hydrate, or carbonate, in hydric nitrate. None are or can be prepared by precipitation, for all nitrates are soluble, like the corresponding chlorates. Their formulæ will readily occur to the student, who should, however, write out a list of them with their names.

Three typical ones are, $K'NO_3$, $Pb''(NO_3)_2$, $Bi'''(NO_3)_3$. Prepare and crystallise these three salts, the first by neutralising hydric nitrate with potassic carbonate; the second by using oxide of lead (litharge); and the third by dissolving the metal.

236. In preparing potassic nitrate, try to make an acid salt in the same way as you prepared hydro-potassic sulphate. You will not succeed,—on evaporating the half neutralised solution,

all the hydrogen nitrate which has not had its hydrogen replaced by potassium, will volatilise and leave neutral potassic nitrate, $K N O_3$, behind. This proves that hydric nitrate is not bibasic.

237. Silver nitrate, $Ag N O_3$, is an exceedingly important body; it is the principal reagent of photography, has considerable applications in surgery (under the name of "lunar caustic"), and is an indispensable reagent in all laboratories. It is prepared by dissolving pure silver in pure hydric nitrate, evaporating to dryness, and cautiously fusing to expel all excess of the hydrogen salt, and then crystallising from water.

238. All nitrates are decomposed by heat, in such a way in most cases, that the oxide of the metal is left.

Heat in a porcelain crucible placed over a lamp as shown in fig. 1, small quantities of

1. Cupric nitrate, $Cu (N O_3)_2$. Cupric oxide, $Cu O$, will be left as a black powder; nitrogen, combined with some of the oxygen as nitric tetroxide, $N_2 O_4$, and free oxygen will escape.

2. Baric nitrate, $Ba (N O_3)_2$ when heated for a considerable time yields baric oxide, $Ba O$; the formation of which can be shown by dissolving the cold mass in water, filtering and showing that the solution is strongly alkaline.

3. Silver nitrate, $Ag N O_3$, which decomposes entirely, leaving metallic silver.

239. The composition of hydric nitrate could be proved thus—

A known weight of pure hydric nitrate, say ·63 grammes, is weighed out—diluted with water, and shaken up with excess of silver oxide—the reaction which then takes place is

$$Ag_2 O + 2 H N O_3 = H_2 O + 2 Ag N O_3.$$

The portion of silver oxide not dissolved is filtered off, and washed with manifold precautions to avoid loss; the filtrate and washings evaporated to dryness in a tared* basin; and the silver nitrate weighed. In the case supposed, we should obtain 1·7 grammes of silver nitrate. This silver nitrate is then placed in a weighed porcelain boat, which is put near the end of a 30 inch length of combustion tube (just under (2) in fig. 56), the front part of which is filled with copper turnings, and put in connection with a pneumatic trough filled with mercury (not shown in fig. 56) by means of a delivery tube, while the end next the boat is attached to an

* *i.e.*, of which the 'tare' or weight, when empty, is known.

apparatus for evolving carbonic dioxide from marble and hydric chloride. All the air is swept out of the tube by a current of carbonic dioxide, and then a large graduated receiver, filled with mercury and a strong solution

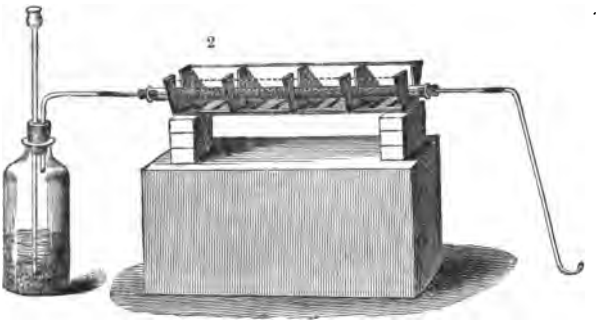


Fig. 56.

of potash, K H O, is supported over the end of the delivery tube. Bubbles of carbonic dioxide rise through the mercury into the potash above it, and immediately combine, and disappear if free from air ($C O_2$ is an *acid* gas, and therefore combines with alkalies). The copper is then raised to redness by burning charcoal (or gas), and lastly the silver nitrate is gradually heated till entirely decomposed. The gaseous products of its decomposition in passing over the ignited copper lose all their oxygen, and nothing escapes into the receiver except a mixture of carbonic dioxide (which is not decomposed by the copper) and nitrogen. As the $C O_2$ entirely dissolves, the gas which collects is pure nitrogen, the volume of which being observed, its weight can be calculated. In this case, it would be ·14 grammes. The little boat with its silver is withdrawn and weighed, when it is found that it contains 1·08 grammes of silver. The weight of the silver and nitrogen found being subtracted from that of the silver nitrate employed, will obviously give that of the oxygen in the salt;

$$1·7 - (1·08 + ·14) = ·48, \text{ the weight of the oxygen;}$$

but the weights of oxygen and nitrogen so found were contained in the original ·63 grammes of hydric nitrate, and $·63 - (·48 + ·14) = ·01$, which is evidently the weight of the hydrogen in that hydric nitrate. Multiplying all these numbers by ten, we see that 63 parts of hydric nitrate contain—1 part of hydrogen, 14 of nitrogen, and 48 of oxygen.

240. The presence of a nitrate in solution is readily detected by either of the following tests:—

1. To the suspected liquid add *half* its bulk of hydric sulphate, to

ensure any nitrate present being in the form of hydric nitrate. To the still warm liquid add a pinch of copper filings (foil or turnings do not answer well). The production of ruddy fumes in the upper part of the tube is evidence of the presence of a nitrate (bromides and nitrites being absent).

2. To the suspected liquid add rather more than its own bulk of hydric sulphate, for the same purposes as before, and to combine with most of the water present. *Cool* the mixture completely, and pour on to its surface a solution of ferr*ous* sulphate, $FeSO_4$, in such a manner as to float on the dense liquid first formed. If the least trace of a nitrate or nitrite be present, a brown layer will be found at the junction of the two liquids. Note, the brown colour is owing to the solution of nitric oxide, N_2O_2, in the ferrous sulphate, see § 258.

241. Nitrates generally, including hydric nitrate, give up oxygen pretty readily to other things which have a tendency to combine with that element, and are consequently used to supply that element to bodies which are to be burnt out of contact with air.

Make a mixture of one part of charcoal, three of nitre, and half of sulphur; put it in a crucible stood in a plate of water, cover the crucible with a bell jar, having a neck (like that used for burning iron wire in oxygen, p. 10); fill the jar with carbonic dioxide by displacement, and touch the mass with a red hot iron. It will burn in a most vigorous manner. The charcoal gets its oxygen from the nitre. Note, one gramme of charcoal will be enough to use. All the materials must be finely powdered, and then well mixed.

The nitrogen of the nitrates of potash and soda is in a form very readily taken up by plants, therefore these salts are useful as manures.

242. In a similar manner gunpowder burns in the chamber of a gun, or the composition in a rocket. Gunpowder contains about 75 parts nitre, 13 parts charcoal (carbon), and 12 parts sulphur, in a hundred. When it burns, the carbon becomes carbonic dioxide (CO_2), the nitrogen of the nitre is liberated, while the sulphur mainly unites with the potassium. The gases are produced at a very high temperature, and consequently are much expanded. If the gases are produced in a confined space, they of course press outwards with a force proportional to their degree of compression, and if any part of the walls of the chamber be moveable, it will be driven away.

243. Hydric nitrate, when submitted to the action of dehydrating agents, does not lose the element of water; but, nevertheless, a body which bears to it the same relation that SO_3 bears to H_2SO_4 (see § 180) can be obtained.

When perfectly dry chlorine gas is passed through a tube containing dry silver nitrate, silver chloride is formed, oxygen liberated, and a silky white mass of crystals deposited in the further end of the tube. These crystals have the composition N_2O_5. The reaction which gives rise to them is—

$$4\,AgNO_3 + 2\,Cl_2 = 4\,AgCl + O_2 + 2\,N_2O_5.$$

$N_2O_5 = 2\,HNO_3 - H_2O$, and is therefore called anhydrous nitric acid. When thrown into water it reproduces ordinary hydric nitrate.

$$N_2O_5 + H_2O = 2\,HNO_3.$$

244. If N_2O_5 (nitric pentoxide) could be deprived first of one atom of oxygen and then of another, and so on till only one atom was left combined with the nitrogen, we should obtain the following series of oxides, including the starting point :—

N_2O_5	called	nitric	pentoxide,
N_2O_4	,,	,,	tetroxide,
N_2O_3	,,	,,	trioxide,
N_2O_2	,,	,,	dioxide,
N_2O	,,	,,	protoxide.

They all exist, and with the exception of the first, are made by the more or less complete deoxidation of hydric nitrate ; which, as we have seen, is closely related to N_2O_5, the first term. This deoxidation is effected in a variety of ways, many being very indirect.

Nitric tetroxide. Nitric peroxide. Hyponitric acid (very bad name).

$N_2O_4 = 92 = 4$ vol., or

23	23
23	23

245. Powder and dry a couple of ounces of lead nitrate, $Pb(NO_3)_2$. When thoroughly dry, place it in a small non-tubulated retort, the bottom of which is coated with Stourbridge clay.* Connect the neck of the retort with a tube formed as shown in the figure, after having put a loose plug of asbestos in its mouth. Apply a gradually increasing heat till low redness is reached. The salt will melt, and then begin to decompose. Deep red vapours will be given off, and will pass into the tube. Now surround the lower part of the latter with a mixture of powdered ice and salt. A liquid will condense in the tube, and a gas capable of re-igniting a glowing splint will escape from the drawn-out end. After a time replace the first tube by a second, and continue the application of heat to the retort till no more liquid condenses in the collecting tube. As each collecting tube becomes three-quarters full, seal it at the contracted portions by the blowpipe.

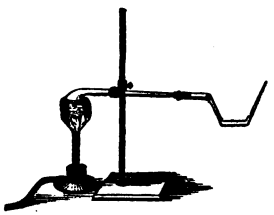


Fig. 57.

246. Lead oxide is left in the retort, the liquid in the sealed tubes consists of nitric peroxide (the last portions being purest), and the gas which escapes during the operation is oxygen. If the nitric tetroxide be quite free from water it appears as a solid. Knowing the results of the decomposition, we can of course easily construct an equation representing it, thus—Lead nitrate is $Pb(NO_3)_2$, and lead oxide PbO, and the difference is N_2O_5, which equals $N_2O_4 + O$; therefore the equation of the reaction is $Pb(NO_3)_2 = PbO + O + N_2O_4$, which must, however, be doubled, in order to avoid having a single atom of oxygen (see § 62).

247. Break off the point of one of the collecting tubes while it is still cold, and pour the liquid into a dry bottle. It will immediately begin to pass into the state of gas if the air be not very cold, and the bottle will become filled with a deep red gas, which is heavier than air, and which is soluble (with decomposition) in water. The purest portions of the condensed tetroxide are of a pale yellow colour when cold, but as the tubes containing them get warmer, the liquid gets darker and darker

* For method of doing this, see Appendix.

in colour till it acquires a rich orange-brown colour. If the liquid is cooled very strongly it becomes a solid.

248. The vapour density of nitric tetroxide, when taken in the usual way, at a temperature considerably over the boiling point of the liquid, is 23 times that of hydrogen; but if its molecular weight be taken as 92; this shows that the molecule occupies 4 volumes.

$$\begin{aligned} N_2 &= 28 = 2 \text{ vol.} \\ O_4 &= 64 = 4 \text{ vol.} \\ \hline N_2O_4 &= 92 = 4 \text{ vol. } \therefore \text{ 1 vol.} = 23. \end{aligned}$$

If its vapour density be taken at temperatures as low as are consistent with its retaining the gaseous form, the number expressing that density is found to be greater, and to approach that required to show that the tetroxide has a normal volume, *i. e.*, two volumes.

249. Nitric tetroxide is the most stable of all the oxides of nitrogen, and results from strongly heating any of the others. It is not decomposed by a red heat, and is devoid of acid characters.

Nitric trioxide. Nitrous acid.

$$N_2O_3 = 76 = 2 \text{ vol. or } \boxed{38 \mid 38}.$$

250. When hydric nitrate is boiled with starch or arsenic trioxide (As_2O_3), a deep-red gas, not to be distinguished in appearance from the tetroxide, is given off; the reaction in the last case being,

$$As_2O_3 + 2\,HNO_3 + 2\,H_2O = 2\,H_3AsO_4 + N_2O_3.$$

When cooled strongly, the gas condenses into a blue liquid, which is decomposed by water, yielding hydric nitrate and nitric dioxide.

When the gas is passed into a solution of potash or soda, a nitr*ite* is formed; it is, therefore, an acid oxide,

$$N_2O_3 + 2KHO = 2KNO_2 + H_2O.$$

251. If potassic or sodic nitr*ate* be fused in a crucible and heated pretty strongly, oxygen will be given off, and potassic or sodic nitr*ite* left.* The heating must not be continued after it is found that a small portion of the mass removed from the crucible and dissolved in water is decidedly alkaline, or the nitrites will be reduced to the state of oxides.

The metallic nitrites are readily decomposed by most hydrogen salts, with temporary production of hydric nitrite, HNO_2, which, however, immediately decomposes, yielding nitric oxide, N_2O_2, and hydric nitrate. Silver nitrite is very slightly soluble.

Nitric dioxide. Nitric oxide. Deutoxide of nitrogen.

$$N_2O_2 = 60 = 4 \text{ vol. or } \begin{array}{|c|c|}\hline 15 & 15 \\ \hline 15 & 15 \\ \hline \end{array}.$$

252. This is a very common product of the deoxidation of hydric nitrate by metals.

Put about two ounces of copper turnings into such a bottle as is used for the preparation of hydrogen, but of smaller size, as shown in fig. 58; pour on them a small quantity of water, and then add hydric nitrate through the funnel. At first the action will be slow, but after a time the liquid will get warm, and then a gas will be given off pretty regularly, if more hydric nitrate be added from time to time. After allowing the air in the generating bottle to escape, collect the gas in bottles or cylinders at the pneumatic trough.

253. Observe that it is perfectly colourless. In the generating bottle a deep-blue solution of nitrate of copper is left. Now let us find out in this case what the reaction must have

* Nitr*ous* acid gives nitr*ites* as sulphur*ous* acid gives sulph*ites*.

been, granting that the gas = N_2O_2. We started with hydric nitrate, HNO_3, and copper Cu″, and ended with nitric oxide and cupric nitrate, Cu″ $(NO_3)_2$ at least. Now N_2O_2 obviously cannot come from less than two molecules of HNO_3, and $2HNO_3$ may be considered as N_2O_5, H_2O (see § 243). Dismissing the water from consideration for the present, we see that N_2O_5 differs from N_2O_2 by O_3, which is what we have to remove from $2HNO_3$ in order to get N_2O_2. To combine with this oxygen, we must use three atoms of copper, because cupric oxide is CuO; we, therefore, get three molecules of cupric oxide. But this cupric oxide is of course formed (if it, indeed, *actually* comes into existence) in presence of hydric nitrate hitherto unacted on; and as the reaction of hydric nitrate on cupric oxide is

Fig. 58.

$$CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O,$$

six molecules of hydric nitrate will be required to convert the three of cupric oxide into cupric nitrate. So we find that for our reaction we require three atoms of copper and eight of hydric nitrate.

$$3Cu + 8HNO_3 = 3\{Cu(NO_3)_2\} + 4H_2O + N_2O_2.$$

254. But we may also explain the reaction in the same sort of way as in the case of the reduction of hydric sulphate by copper in getting SO_2, *i. e.* by supposing that the metal first replaces an equivalent quantity of hydrogen from the hydrogen salt, and that that hydrogen, while nascent, reduces some of the excess of the hydric nitrate present. Here three atoms of copper would displace six atoms of hydrogen, which in its turn would combine with the three atoms of oxygen out of two molecules of hydric nitrate. This second view is supported by the fact that

there is *always* some ammonia formed during this reaction (read this statement by the light of §210).

255. Nitric oxide supports the combustion of bodies which burn vigorously, but not that of things which do not, because it requires a high temperature to decompose it.

With gas which has been prepared slowly, try these experiments :—

Introduce into a bottle of the gas a wax candle burning brightly :—if the gas is pure, the candle will continue to burn with a peculiar but very bright flame. Into another put a bit of burning phosphorus in a deflagrating ladle :—it will burn as brightly as in oxygen. Into a third put a lighted splinter of wood :—it will be extinguished.

256. In performing these experiments, it will be remarked that, as soon as a bottle of the gas is opened, deep-red fumes will be formed where it meets the air. They are caused by the N_2O_2 uniting with oxygen to form N_2O_3 and N_2O_4. This most interesting and valuable property of N_2O_2 can be well exhibited by slowly passing bubbles of oxygen up into a jar of the gas standing over water. As each bubble enters, it forms a deep-red cloud, which quickly disappears; the water rising in the jar at the same time. By adding the oxygen slowly, the whole of the gas may be made to dissolve.

The progress of diffusion of one gas into another can also be very prettily seen by filling the diffusion tube shown in fig. 25 with this gas.

257. Nitric tri- and tetroxides are sometimes prepared by mixing nitric dioxide with the proper proportion of oxygen, and cooling the mixture very strongly, so as to condense the product.

$$2\,N_2O_2 + O_2 = 2\,N_2O_3$$
$$N_2O_2 + O_2 = N_2O_4.$$

258. Pass a few bubbles of nitric oxide into a solution of ferrous sulphate ($FeSO_4$), the gas will be absorbed, and the liquid will be turned almost black. Heat together in a flask ½ oz. commercial hydric nitrate and a *strongly acid* solution of 2 oz. of ferr*ous* sulphate. Collect the gas which is given off, you will find it to be nitric oxide. The ferrous sulphate

becomes ferric sulphate, $Fe_2 O_3$ 3 S O_3, at the expense of the oxygen of the hydric nitrate, which is, therefore, reduced to nitric oxide. By the light of the last two experiments explain the mode of operation of the ordinary

Fig. 59.

test for the presence of nitrates (§ 240). The apparatus to be employed for this experiment is shown in fig. 59, which represents the passage of the gas into a solution of ferrous sulphate.

259. Nitric oxide has a density only fifteen times as great as hydrogen,

$$N_2 = 28 \doteq 2 \text{ vol.}$$
$$O_2 = 32 = 2 \text{ vol.}$$
$$N_2 O_2 = 60 = 4 \text{ vol. } \therefore \text{ 1 vol. } = 15,$$

so that it affords another instance of anomalous vapour volume. By taking N O as its molecular formula, we should remove this anomaly at the expense of ignoring the facts that by addition of an atom of oxygen it forms $N_2 O_3$ (the formula for which cannot be halved), and that by abstraction of an atom of oxygen from it by moist iron or hydric sulphite (see nitrous oxide) it gives $N_2 O$ nitrous oxide, the formula of which cannot be divided.

260. As further examples of methods of calculation—

Let it be required to know what weight of copper must be used in order to prepare 13 grammes of nitric oxide. Our equation $3\ Cu + 8\ H N O_3 = 3\ \{Cu\ (N O_3)_2\} + 4\ H_2 O + N_2 O_2$, states that a quantity of copper represented by 3 Cu is required to furnish a quantity of nitric oxide represented by $N_2 O_2$. Now the atomic weight of copper is 63·5, therefore, $3\ Cu = 63{\cdot}5 \times 3 = 190{\cdot}5$, and $N_2 O_2 = (14 \times 2) + (16 \times 2) = 60$. So

to get 60 parts (say grammes) by weight of N_2O_3, we must employ 190·5 parts of copper, so

$\therefore$ 60 grammes N_2O_3 requires 190·5 of copper

$\therefore$ 1 ,, ,, ,, $\frac{190{\cdot}5}{60}$

$\therefore$ 13 ,, ,, ,, $\frac{190{\cdot}5}{60} \times 13 = 41{\cdot}275$ grammes.

Work out in the same way the quantities of hydric nitrate required and of nitrate of copper formed in the preparation of the same quantity of nitric oxide.

261. Let it also be required to know,—how many cubic centimetres the 13 grammes of nitric oxide will occupy at 0° C. and 760 millim. barometric pressure.

Because $N_2O_2 = 60$, and is a four volume gas (*i.e.*, its molecular weight expressed in any unit occupies four times the volume of the atomic weight of hydrogen expressed in the same units), one volume of it must weigh 15. But our unit of weight here is the gramme, and 1 gramme of hydrogen (under conditions given) occupies 11·2 litres, *i.e.* 11200 cubic centimetres. Therefore, 15 grammes of N_2O_2 occupy 11200 cubic centimetres, and, therefore, 13 grains will occupy $\frac{13}{15}$ of 11200 cubic centimetres.

Nitric protoxide. Nitrous oxide. Laughing gas,

$N_2O = 44 = 2$ vol. or | 22 | 22 |

262. This body is most conveniently made by simply heating ammonic nitrate (NH_4NO_3).

Put about four ounces of this salt into a flask fitted with a cork and delivery tube. Apply heat gently. The salt will melt, and then appear to boil, and a gas will be given off, which may be collected either over hot water or by downward displacement. (In the last case it must be passed through an empty washing bottle standing in a pan of cold water, in order to condense the steam which accompanies it, as shown in fig. 60). If the application of heat be continued, the whole of the salt will be decomposed, and nothing be left in the flask.

The reaction is

$$N H_4 N O_3 = N_2 O + 2 H_2 O,$$

that is, the hydrogen of the ammonium unites with two-thirds of the oxygen in the salt, and both atoms of nitrogen go off

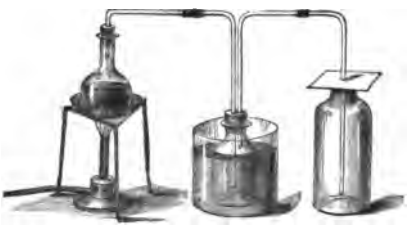


Fig. 60.

with the other. This is the only practicable way of preparing the gas.*

263. It may be made by depriving nitric oxide of one-half of its oxygen by the action of such reducing agents as moist iron filings or hydric sulphite. The reaction in the last case is $S O_2, H_2 O + N_2 O_2 = N_2 O + H_2 S O_4$. To employ this method, which is very interesting—

Fill a large wide-mouth stoppered bottle, containing two or three ounces of a saturated solution of sulphuric dioxide, with nitric oxide by displacement,† close it with its well-greased stopper, and set aside for five or six hours. Then open it under the surface of water containing potash in solution. This last will absorb the excess of "sulphurous acid," and after agitation of the gas with the alkaline solution, you will find about half the original volume of gas left. $N_2 O_2 - O = N_2 O$, but $N_2 O_2 = 4$ vol., and $N_2 O = 2$ vol. This will no longer have the power to give red fumes with air, and will exhibit the properties of nitr*ous* oxide.

264. Nitrous oxide dissolves in rather less than its own volume of cold water. It can be condensed to a liquid by

* Use pure ammonic nitrate, and heat gently.

† It will be necessary to evolve the gas very quickly for this purpose, since the specific gravity of $N_2 O_2$ is only $\frac{15}{14{\cdot}4}$, see § 259.

a pressure of thirty atmospheres at 0° C., and this liquid can be frozen into a solid by the cold produced by its own evaporation. The gas is perfectly colourless, and has so slight a smell, that when breathed it only gives a sensation of slight sweetness. Its density, as compared with hydrogen, is 22.

$\therefore N_2O = 44 = 2$ vol.; as compared with air, $\frac{22}{14{\cdot}4} = 1{\cdot}52$.

It supports combustion almost as readily as oxygen, as shown by its relighting a glowing splint, and by the manner in which a candle, a bit of phosphorus, &c., will burn in a jar of the gas. Sulphur burns in it with a peculiar pink-edged flame. When phosphorus is burnt in it, red fumes make their appearance, owing to the great heat, which resolves a portion (a small one) into free nitrogen and nitric tetroxide,

$$4\,N_2O = 3\,N_2 + N_2O_4.$$

265. It is distinguished from oxygen by observing, 1st, that it is much more soluble in water; 2ndly, that it is not absorbed by pyrogallate of potash; and 3rdly, that it gives *no* red fumes when mixed with nitric oxide, N_2O_2. As this is the only oxide of nitrogen which could be mistaken for oxygen, this last test shows that the oxygen in air is uncombined. It has received the name of laughing gas, because when it is inhaled it produces a kind of intoxication, accompanied in some cases by a tendency to violent laughter. No one should venture to attempt this experiment without the sanction of a medical man, as it might lead to fatal consequences. It is sometimes used to produce a temporary insensibility to pain.

266. That these various oxides of nitrogen have the compositions assigned to them could be proved by passing known quantities of them over a weighed quantity of metallic copper, and collecting the nitrogen which would in all cases result. The increase in weight of the copper would give the quantity of oxygen contained in the weight of the particular oxide experimented with, and the volume of nitrogen obtained would give the weight of that element by calculation.

267. The existence of this series of oxides of the same element is a principal evidence in favour of the "Atomic Theory." The same quantity of nitrogen (28 parts) combines successively with 16 parts, 16 × 2, 16 × 3, 16 × 4, and 16 × 5 parts of oxygen, and with *no intermediate* quantities, which seems to show past all question that the smallest quantity of oxygen which can enter into combination with 28 parts of nitrogen is 16 parts. Of course, if 28 parts of nitrogen will combine with 16, 16 × 2, &c., parts of oxygen, 1 part of nitrogen will form compounds with $\frac{16}{28}$; $\frac{16 \times 2}{28}$, &c., parts of oxygen: still the proportions remain unaltered, and we are compelled to imagine that there is a practical limit to the divisibility (in a chemical sense) of oxygen, or otherwise there seems no reason why we should not have a compound of, say, 28 parts of nitrogen with 4·5, or any other quantity of oxygen, or, indeed, why they should not combine in any proportions whatever.

QUESTIONS ON CHAPTER XI.

1. How do nitrates originate?
2. What is the formula for hydric nitrate, and by what other name is it known?
3. Describe in detail the preparation of hydric nitrate.
4. (*a*) What weight of hydric nitrate can be obtained by acting on 500 grammes of potassic nitrate by hydric sulphate?—*Ans.* 311·8 grammes.

(*b*) What weight of hydric sulphate would be required if the operation had to be performed in a glass vessel?—*Ans.* 485·148 grammes.

5. Describe the appearance and properties of hydric nitrate. Describe the experiments which illustrate its properties.
6. What metals are not attacked by hydric nitrate?
7. What phenomenon attends the solution of most metals in hydric nitrate?

8. How would you prepare the nitrates of silver, copper, lead, mercury, potassium? Give the formula for each salt.

9. What is the action of heat on the nitrates?

10. How could it be proved that the elements of hydric nitrate are united in the proportions represented by its formula?

11. How is the presence of a nitrate detected?

12. What is the use of the "saltpetre" in gunpowder?

13. What is formed when dry chlorine is passed over dry silver nitrate? What relation does it bear to hydric nitrate?

14. How many oxides of nitrogen are there? Name each, and give its symbol.

15. (*a*) What is formed when nitrate of lead is heated? (*b*) Give the equation representing the change. (*c*) Name the chief properties of the vapour given off.

16. What is there remarkable about the vapour volume of nitric tetroxide?

17. What volume of oxygen is contained in a litre of nitric tetroxide?—*Ans.* 1 litre.

18. How is nitric trioxide prepared? Why is it also called nitrous acid?

19. When "nitrous acid" forms salts, how are these distinguished (verbally) from those given by "nitric acid"?

20. What action takes place when dilute hydric nitrate is poured upon copper? Describe the gaseous compound. What weight of copper must I use to get 100 grs. of the gas?—*Ans.* 317·5 grammes.

21. What is the most characteristic property of binoxide of nitrogen? For what purposes is this property made use of?

22. Explain the mode of action of the ordinary test for the presence of nitrates.

23. If 11·2 litres of nitric oxide were passed over a weighed quantity of red hot metallic copper, what increase of weight would the copper undergo?—*Ans.* 8 grammes.

24. What would be the weight of 1 litre of nitric oxide?—*Ans.* 1·34 grammes.

25 (*a*) What is formed when nitrate of ammonia is heated? (*b*) Give the equation representing the change. (*c*) Name the chief properties of the gas.

26. What weight of ammonic nitrate must be decomposed in order to yield 5·6 litres of the gas?—*Ans.* 20 grammes.

27. What are the properties of nitrous oxide, and how can it be distinguished from oxygen?

28. What is the specific gravity of "laughing gas"?—*Ans.* 1·53 nearly.

29. What weight of suphur could be burnt by a litre of nitrous oxide?—*Ans.* ·714 grammes.

30. How does hydric nitrate act on silver, antimony, and gold?

31. In what respects do nitrates and chlorates resemble each other?

32. What proof can you give that hydric nitrate is not bi- or tri-basic?

CHAPTER XII.

PHOSPHORUS.—Symbol P. Atomic weight 31.

Combining volume $\frac{1}{2}$ or $\boxed{31}$ $P_4 = 2$ vol. $= 124$.

268. This element, which is the second term of the nitrogen group of elements, never occurs in the free state in nature, but always in the form of some compound, generally as a phosphate. Phosphate of lime occurs in small quantity in all soils, and is taken up by plants which, consequently, always contain more or less phosphorus in the form of phosphates. Animals derive from the plants (directly or indirectly), all the phosphorus which goes to form the phosphate of lime, of which the hard part of their bones consists. Most of the other tissues of animals also contain phosphorus in some form or other.

269. Bones consist of two parts, one animal, and the other mineral, as can be shown thus,—

Soak a long bone of some animal in a jar of dilute hydric chloride for some days. Its appearance will be but little altered, but it will have become flexible, owing to the removal of the stiffening earthy body originally contained in it. To some of the acid liquid in which the bone has been soaked add ammonia; a white precipitate of the original earthy matter will be thrown down; it consists of phosphate of lime. Rasp up a bit of bone and ignite it on the lid of a porcelain crucible: at first it will blacken and then become white again. The blackening is caused by the charring of the animal matter, and the whitening by the reappearance of the natural colour of the calcic phosphate when the animal matter is completely burnt away.

270. Phosphorus is always extracted from bones. The method of doing so is somewhat intricate and difficult to follow,

and indeed will not be found easy to be understood till the phosphates have been studied.

Bones are calcined till the whole of the animal matter has been burnt away, and the phosphate of lime is left as a white ash (bone ash), which has the composition $P_2O_8Ca_3$.* This is then mixed with two-thirds of its weight of oil of vitriol (H_2SO_4) diluted with about twice its weight of water; the whole is allowed to stand for twenty-four hours, then mixed with more water, and the liquid strained off from the bulky white residue. The action of the hydric sulphate is the ordinary one which it exerts on metallic salts, *i.e.*, it is a replacement of the metal by hydrogen, only in this case the replacement is not complete.

$$P_2O_8Ca_3 + 2\,H_2SO_4 = P_2O_8H_4Ca + 2\,CaSO_4$$

The calcic sulphate is nearly insoluble, while the *superphosphate of lime* is soluble; therefore the clear liquid contains all the phosphorus in the bone ash employed. The liquid is boiled down to a small bulk, and when quite thick is mixed with a large quantity of powdered charcoal, and the mass so obtained is then heated almost to redness in order to render it quite dry. By the action of heat, tetra-hydrocalcic-diphosphate (superphosphate of lime) is resolved into water, which goes off, and calcic metaphosphate, CaP_2O_6,

$$P_2O_8CaH_4 = 2\,H_2O + CaP_2O_6.$$

The dry residue is introduced, while quite hot, into earthenware retorts; these are heated in a furnace, and the evolved vapours of phosphorus passed through a wide copper pipe into a vessel of water. The phosphorus condenses and falls to the bottom of the water, as waxy-looking drops. The reaction which occurs in the retort is this:

$$3\,CaP_2O_6 + 10\,C = Ca_3P_2O_8 + 10\,\underbrace{CO}_{\text{carbonic oxide.}} + P_4,$$

i.e., the carbon (charcoal) robs the calcic phosphate of some of its oxygen. Of course, at the end of the operation the retort contains the tricalcic phosphate and any excess of carbon which may have been used. The manufacture of phosphorus cannot be carried out in an ordinary school laboratory. The phosphorus which collects in the receivers is melted under hot water, and while still there is squeezed through chamois leather in order to remove dirt, and is then cast into sticks.

271. In performing the experiments described in this chapter,

* Neglecting impurities, which form but a small proportion of the whole.

be *very* careful to avoid exposing phosphorus for a long time to the air, or rubbing, striking, or handling it when above the surface of water, or it may catch fire. Observe, that it is a wax-like solid, almost transparent (when freshly made, and not exposed to sunlight, or if fresh surfaces be made to it by cutting), soft enough to be easily indented by the nail, cuts without difficulty, is somewhat flexible, and melts below water when the temperature rises above 44° C. If you try this, put the phosphorus in a test tube of water, and plunge the latter into another vessel containing warm water. It boils about 290° C., giving a vapour of the density 62 times as great as that of hydrogen. Do not attempt to verify the boiling point. The density of solid clear phosphorus is almost exactly the same as that of hydric sulphate, *i. e.* 1·83. Though not soluble in water, it dissolves very readily in carbonic disulphide, and can be crystallised from that liquid; but this is an experiment not to be recommended, for apart from the intolerable smell and injurious effects of the vapour of the liquid, the solution of phosphorus so made, will, if accidentally upset over the operator or any combustible material, ignite spontaneously, and cause severe damage. Phosphorus is also soluble, though to a slight extent, in oil, in ether, and in alcohol.

272. Phosphorus unites readily with oxygen, chlorine, and bromine at ordinary temperatures, producing of course a rise of temperature, which accelerates the action. If phosphorus in a finely divided state be exposed to the atmosphere, it speedily bursts into flame (read over § 50, and apply the reasoning there given to explain this statement). Even when it never attains a sufficiently high temperature to inflame, it gives off a faint light when exposed to air, and has received its name from this circumstance. It is *very* poisonous. Phosphorus is possessed of great reducing power, in consequence of the energy with which it unites with oxygen, chlorine, &c.

Put a stick of phosphorus into a *weak* solution of cupric sulphate ($Cu\,S\,O_4$): the metal will be reduced and deposited on the surface of the phosphorus in the form of a bright coating.

Repeat the experiment, using a solution of silver nitrate instead of copper sulphate—silver will be deposited.

273. Phosphorus, like sulphur, occurs in many forms:—a white variety, produced by the action of light on the clear phosphorus:—a black one, made by suddenly cooling phosphorus which has been heated to some degrees above its melting point:—a viscous one, made by suddenly cooling phosphorus which is near its boiling point:—and a red one, which is of considerable importance.

Red, or amorphous* (?) phosphorus can be prepared thus:

Place an ounce or so of ordinary phosphorus, which has been dried by filter paper, in a small flask furnished with a good cork, and a *long* tube bent as shown in fig. 61, and dipping into mercury. Stand the flask in a bath of linseed oil (a small saucepan forms the cheapest and best oil bath), and hang a thermometer (*t*) in the oil by its side. Allow the whole to stand till the phosphorus has absorbed the oxygen of the air in the flask; and then heat the oil slowly up to about 235° C., and maintain it at that temperature for thirty or forty hours, taking especial care that it never rises as far as 250° C. The phosphorus, which on the first application of heat becomes quite liquid, gradually turns red, and is reduced to a hard mass of a brick-red colour. Even after long heating there will be some unaltered phosphorus left, which must be dissolved out by bisulphide of carbon, or a boiling solution of caustic alkali.

Fig. 61.

274. The red mass, which is so obtained, will vary in shade—with the temperature employed in making it and the fineness to which it is powdered—from deep chocolate to vermilion red. It presents none of the characters, physical or chemical, of ordinary phosphorus, *e. g.*, it is insoluble in bisulphide of carbon, ether, and oils. It is not fusible, and may be heated to 250° C. in the open air without catching fire, but at that temperature it suddenly and violently resumes its ordinary form, and burns with energy. It is heavier than the common kind, as 2 is greater than 1·83. It may be rubbed or struck

* Without form, *i.e.*, without crystalline form.

with impunity, and when exposed to the air, absorbs oxygen *very* slowly if it is not moist. It is not poisonous, and does not reduce a solution of cupric sulphate. It is used in the composition of the striking surface placed on the boxes in which the patent safety matches are sold.

275. A simpler and more expeditious method of preparing red phosphorus is to

Melt the ordinary kind under the surface of strong hydric chloride solution, add a single grain of iodine, and maintain the whole at a temperature of 100° C. by standing the test tube in a pan of boiling water.

276. The vapour density of phosphorus is 62, even when taken at so high a temperature as 1000° C., whence it appears that, if the atomic weight of the element is 31, its molecule (taking the quantity which occupies 2 vols. in a state of vapour, as the measure of the molecule) must consist of 4 atoms. For if 31 grammes of phosphorus, on being converted into vapour, occupy only half the space occupied by 1 gramme of hydrogen at the same temperature, it must require 31×4 grammes to occupy the space of 2 grammes of hydrogen. That its atomic weight is 31, and not 62, as indicated by its vapour density, is shown by the composition and density of its hydrogen compound, $P H_3$.

277. Phosphorus forms three compounds with hydrogen, but only one is of much interest.

Trihydric Phosphide, Phosphuretted Hydrogen, Phosphamine.

Symb. $P H_3$. Molecular weight 34. Combining volume

17	17

When a metallic sulphide is dissolved in dilute hydric chloride or sulphate, sulphuretted hydrogen is produced (§ 146), and similarly if a metallic phosphide is so treated, it gives phosphuretted hydrogen. But it is difficult to prepare a suitable phosphide in a state of sufficient purity, so other methods are resorted to.

Heat hydric phosphite, prepared as described in §§ 285 and 300, in a very small flask furnished with a cork and simple delivery tube. Phosphuretted hydrogen will be given off, and may be collected over water. The reaction which takes place is—

$$\underbrace{4\,P\,O_3\,H_3}_{\text{hydric phosphite.}} = 3\,P\,O_4\,H_3 + P\,H_3.$$

278. So prepared, phosphuretted hydrogen is a colourless gas, having a strong and disagreeable, but very characteristic smell, resembling rotten fish. It burns in the air, when ignited, with a white flame, producing at the same time dense white clouds of hydric phosphate. Though analogous in composition to ammonia, it is very little soluble in water, and does not combine with hydrogen salts with anything like the same energy. Indeed, it is only known to combine with two, viz., hydric iodide and hydric bromide. In preparing hydric iodide by the method described in § 124, a small quantity of transparent crystals appears in the neck of the retort; they have the composition $P\,H_3\,H\,I$, that is, of a hydriodate of phos-amine (phosphorus ammonia). $P\,H_4\,I$ is, however, so unstable that it is decomposed by water. Phosphuretted hydrogen is, therefore, in some degree possessed of the power to unite with acid bodies, which ammonia enjoys to so large an extent, and so makes good its claim to be considered a true analogue of that body.

By passing hydric iodide up into dry hydric phosphide contained in a tube standing over mercury, the union of the two gases is manifested by diminution of volume and production of a white solid. The addition of a few drops of water causes the decomposition of the salt and restores the original volume of the hydric phosphide.

279. It has no action whatever on vegetable colours, notwithstanding its feeble basic power. It is decomposed by a series of electric sparks, or by transmission through a red-hot tube, into free phosphorus and hydrogen. When passed into solutions of metallic salts, it forms precipitates in many cases—with cupric sulphate for example, it gives a precipitate of cupric phosphide.

$$2\,P\,H_3 + 3\,Cu\,S\,O_4 = 3\,H_2\,S\,O_4 + Cu_3\,P_2,$$

a reaction, which may be compared to that of sulphuretted hydrogen on the same salt.

With silver nitrate it gives a precipitate of metallic silver,

$$6\,AgNO_3 + PH_3 + 3\,H_2O = 6\,HNO_3 + H_3PO_3 + 3\,Ag_2.$$

280. Hydric phosphide results from the reduction of hydric phosphite by nascent hydrogen, as hydric nitride (ammonia) results from the reduction of hydric nitrite.

$$H_3PO_3 + H_6 = 3\,H_2O + PH_3.$$

Repeat the experiment described in § 210, substituting a solution of hydric phosphite for the hydric nitrate. The characteristic smell of hydric phosphide will be developed. Further evidence can be obtained of the action, by passing the evolved gas through a solution of silver nitrate, in which a grey precipitate of metallic silver will be formed.

281. PH_3, or more probably P_2H_4, represents the composition of a liquid compound of phosphorus and hydrogen, which is produced in small quantity when phosphorus is dissolved in a boiling solution of caustic alkali, at the same time that a considerable amount of PH_3 is formed. Without attempting the separation of the two compounds, a very pleasing experiment may be thus made. Note. Attend strictly to the directions given, or an accident may occur.

Put a gramme or two of phosphorus into a small non-tubulated retort and then fill this up, neck and all, with a solution of caustic soda, caustic

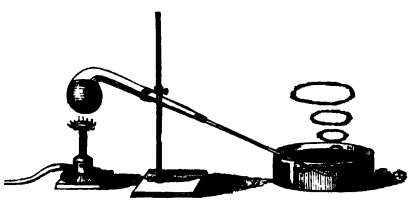


Fig. 62.

potash, or milk of lime. Fit to the neck of the retort a delivery tube, and plunge this last below the surface of water in a good sized pan. Apply a gentle heat; in a short time bubbles of gas will form over the surface of

the melted phosphorus, will rise and gradually expel the liquid from the neck of the retort, and at last escape from the end, rise through the water in the pan, and burst in the air. As each bubble bursts it spontaneously catches fire, and the hydric phosphate formed rises in the shape of a rolling and growing ring of white smoke. In cleaning out the retort, take the precaution to place the thumb over the mouth of the delivery tube before lifting it out of the basin, and then to plunge retort and all entirely below the surface of cold water, while the thumb still remains on the mouth of the delivery tube. Allow the contained gas to escape slowly, and then remove the phosphorus. The admission of air to the retort while gas still remains would result in an explosion.

282. If the escaping gas be passed through a U tube surrounded with a freezing mixture, it deposits a small quantity of a liquid body, and loses its power of spontaneous inflammability. The liquid is P_2H_4; it is spontaneously inflammable, and it is its vapour which causes the phosphuretted hydrogen prepared as above to enjoy the same property. The reaction which gives rise to P_2H_4 is not understood. The main reaction between caustic soda and phosphorus is this,

$$P_4 + 3\,NaHO + 3\,H_2O = PH_3 + \underbrace{3\,PH_2O_2Na.}_{\text{sodic hypophosphite.}}$$

The other compound, P_4H_2, is solid.

CHLORIDES OF PHOSPHORUS.

283. Phosphorus forms two compounds with chlorine, PCl_3, phosphor*ous* chloride or phosphoric trichloride, and PCl_5, phosph*oric* chloride or phosphoric pentachloride; both resulting from the direct union of chlorine and phosphorus. Place an ounce of red phosphorus in a tubulated retort connected with a receiver, pass dry chlorine gas into the retort, and, if necessary, start the action by a gentle heat. The phosphorus will combine with the chlorine without catching fire, and a liquid product (PCl_3) will be first formed, but will soon become solid if chlorine in excess be employed, owing to its taking up a molecule of chlorine (Cl_2) to form PCl_5. When all action has ceased, rake * out about half the product and preserve it

* Be careful to operate in a draught which will carry all fumes from you, as the vapours of this and all the other compounds of phosphorus and chlorine are painfully irritating and injurious.

for use in a well-stoppered bottle; it is PCl_5 in the form of a yellowish-white crystallised mass. To the remainder in the retort add half an ounce of ordinary phosphorus, and heat. This reaction will be set up—

$$6\,PCl_5 + P_4 = 10\,PCl_3$$

and a colourless oily liquid will distil over; it is PCl_3; preserve it. These bodies are very interesting in many ways.

284. PCl_5, when converted into vapour, has only half the density which theory would assign to it. Being a compound, its molecule in a state of vapour *should* occupy twice the space of an atom of hydrogen at the same temperature, but in fact it occupies four times the space. This for a long time caused considerable perplexity to chemists, until it was found that on evaporation it split up into PCl_3, and Cl_2, which, both being complete molecules, occupied their proper space, so that the mixture was equal to 4 volumes.

285. When PCl_3 is thrown into an excess of water it reacts thus:

$$PCl_3 + 3\,H_2O = \underbrace{PO_3H_3}_{\text{hydric phosphite.}} + 3\,HCl,$$

that is, it exchanges 3 Cl for the elements of 3 (H O) hydroxyl (§ 156).

286. When PCl_5 is thrown into water it reacts violently, producing at first an oily body of the composition $POCl_3$ (oxychloride of phosphorus), which sinks to the bottom and then soon disappears. The oxychloride of phosphorus is produced by an exchange of two atoms of monovalent chlorine for one of divalent oxygen.

$$PCl_5 + H_2O = POCl_3 + 2\,HCl.$$

The oxychloride of phosphorus again reacts on water by exchanging its remaining chlorine for hydroxyl.

$$POCl_3 + 3\,H_2O = \underbrace{PO_4H_3}_{\text{trihydric phosphate.}} + 3\,HCl.$$

This, at least, is the received view; some experiments of the author's appear, however, to make another view more probable, viz., that the first action of the water on the pentachloride is repeated, and a body, PO_2Cl, is formed,

$$POCl_3 + H_2O = 2\,HCl + PO_2Cl;$$

and that this body (PO_2Cl) reacts with water to form hydric chloride and monohydric phosphate,

$$PO_2Cl + H_2O = HCl + PO_2H.$$

The consideration of the reactions of pentachloride of phosphorus on other bodies must be deferred.

287. Phosphorus forms two bromides, PBr_3 and PBr_5, analogous to the chlorides, and two iodides PI_3 and PI_5. The iodides are prepared by dissolving iodine in bisulphide of carbon and adding the necessary amount of phosphorus, little by little, to the liquid, kept cold. Both are red solids, and are decomposed by water, with formation of hydric iodide.

OXIDISED COMPOUNDS OF PHOSPHORUS.

288. There are two known oxides of phosphorus, both of which are acid.

P_2O_3, phosphoric trioxide, or phosph*orous* acid, and
P_2O_5, phosphoric pentoxide, or phosph*oric* acid,

which correspond to N_2O_3, and N_2O_5.

Both are made by the direct union of phosphorus and oxygen; the first, P_2O_3, by burning phosphorus in a limited supply of dry air, and the second, P_2O_5, by burning the element in a large excess of air or oxygen. Phosphoric pentoxide is an interesting and useful body, which is best prepared in an apparatus constructed on the *principle* of that shown in fig. 63.

A large glass globe, or, better, a two-gallon wide-mouth stoneware jar, is furnished with a narrow entrance tube, as shown at (*d*), a wide exit tube (*g*), and a wide open tube (*a*) passing straight down from its upper part to immediately over a small earthenware dish or crucible, supported by wire or by standing on another inverted crucible. The entrance tube (*d*) should terminate a few inches from the surface of the dish. A small bit of dry phosphorus is dropped down (*a*) and lighted by a hot wire (*a*), closed, and a brisk current of air forced through (*d*) and its drying tube by means of a pair of bellows. When the first bit of phosphorus is consumed another is dropped in, and so on till enough has been burnt.

Dense white clouds of phosphoric pentoxide will be formed, and will partly settle in the large globe or jar, and partly in the

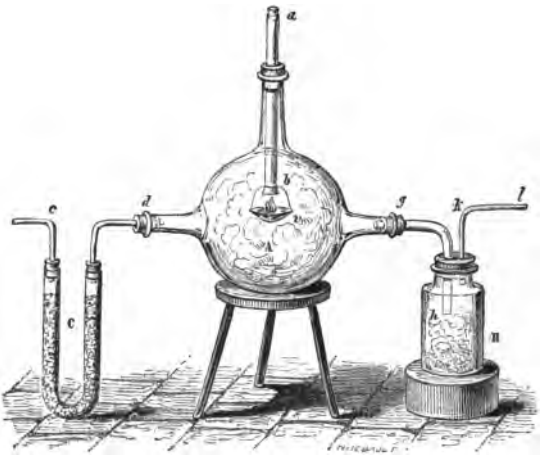


Fig. 63.

bottle (B), attached to the exit tube, in the form of a snow-white powder, which must be immediately shaken out into a sheet of glazed paper and transferred to a well stoppered bottle. If the supply of air has been defective, some of the lower oxide of phosphorus will be mixed with the pentoxide.

Phosphoric pentoxide is the most hygroscopic (water taking) body known, it even takes water from hydric sulphate, § 179. It is sometimes used to render gases perfectly dry in very refined experiments.

289. P_2O_5, when thrown into water reacts on that body with extreme violence, making a hissing noise like a red hot metal, and produces a hydrogen salt, having the composition HPO_3, corresponding in composition to HNO_3.

$$P_2O_5 + H_2O = 2\,HPO_3,$$

phosphoric pentoxide is, therefore, "anhydrous phosphoric acid,"

—and $H P O_3$, is "(mono) hydrated phosphoric acid," or hydric phosphate (compare with $N_2 O_5$ and $H N O_3$). If the solution of hydric phosphate be evaporated to dryness and ignited in a platinum dish, an ice-like mass is obtained on cooling. This kind of "phosphoric acid" has therefore received the name "glacial phosphoric acid." Its neutralised solutions give a *white* precipitate of $Ag P O_3$ with nitrate of silver, and the hydrogen salt itself coagulates albumen (the white of egg). When neutralised with alkalies it gives salts with the general formula $M' P O_3$, corresponding to the nitrates, but much less soluble as a rule.

NOTE.—As $H P O_3$ so readily becomes $H_3 P O_4$ (see next §), the action of water on $P_2 O_5$ always produces some of the latter; but only a very little of the temperature is not allowed to rise.

290. When a solution of monohydric phosphate is boiled for some time (an hour or two; the action is quicker if a small quantity of hydric sulphate be present), then neutralised and tested with silver nitrate, a *yellow* precipitate is obtained, and if this be analysed, it is found to have the composition $Ag_3 P O_4$. Now how can this have come about? We have seen that metallic salts are produced by replacing the hydrogen in a hydrogen salt, by the equivalent quantity of some metal. As silver is monovalent, the hydrogen salt corresponding to $Ag_3 P O_4$, must have been $H_3 P O_4$, which obviously differs from $H P O_3$ by the elements of water, $H_3 P O_4 = H P O_3 + H_2 O$; therefore, when monohydric phosphate (glacial phosphoric acid) is boiled with water, it *combines* with one molecule of that body, and forms trihydric phosphate.

291. Trihydric phosphate results also from the action of water on phosphoric chloride, as before shown. It can also be made thus,—

Dilute commercial "nitric acid" (hydric nitrate) with its own bulk of water, boil it in a stoppered retort, and drop in small pieces of phosphorus, taking care not to add another bit till the first is dissolved, and also to avoid letting the phosphorus touch the hot retort before it enters the liquid. The phosphorus will be oxidised at the expense of the nitrate, red fumes will escape, and hydric phosphate will remain in the body of the retort dissolved in the excess of hydric nitrate, which has not distilled out into

the receiving flask. By cautious evaporation in a dish the nitrate can be expelled, and the nonvolatile phosphate left; but

As trihydric phosphate loses the elements of water very readily, so as to give monohydric phosphate, it is difficult to avoid going too far, and converting some into monohydric phosphate, and it may be necessary to boil the product for some time with water, in order to restore it to the trihydric state.

Trihydric phosphate is an exceedingly definite body, which can be obtained in crystals, and which is so stable, that it is destitute of oxidising power, and is not reducible by nascent hydrogen. It is strongly acid, has a pure sour taste, and is not poisonous.

292. Trihydric phosphate and the metallic salts corresponding to it are much commoner than the other phosphates, and are called orthophosphates.

293. As trihydric phosphate contains three atoms of hydrogen, and as all three are replaceable by metals (witness Ag_3PO_4), three series of salts can be prepared from it.

$$\left.\begin{matrix} H \\ H \\ M' \end{matrix}\right\} PO_4 \qquad \left.\begin{matrix} H \\ M' \\ M' \end{matrix}\right\} PO_4 \qquad \left.\begin{matrix} M' \\ M' \\ M' \end{matrix}\right\} PO_4$$

If M′ stand for one of the alkali metals (K Na or NH_4), the first series will be acid in reaction, the second faintly alkaline, and the third very strongly alkaline.

The ordinary phosphate of soda of commerce, or rhombic phosphate of soda, which has the composition of HNa_2PO_4 (omitting water of crystallisation) is the best preparation to use for examining the properties of the phosphates. By adding caustic soda to it and crystallising, Na_3PO_4 may be obtained—

$$Na_2HPO_4 + NaHO = Na_3PO_4 + H_2O,$$

or by adding to it a solution of trihydric phosphate and crystallising, H_2NaPO_4 results—

$$Na_2HPO_4 + H_3PO_4 = 2\,NaH_2PO_4.$$

294. The normal * phosphates of the heavy metals, and of the alkaline earthy ones, are insoluble in water, but soluble in hydric chloride or nitrate; we can, therefore, prepare them by precipitation if we avoid having the liquid acid.

Add a solution of nitrate of silver to a solution of hydrodisodic phosphate, you will obtain a bright yellow precipitate, but on testing the supernatant liquid with litmus paper you will find it acid, though the silver salt used was neutral, and the soda salt slightly alkaline. This arises from the fact (so valuable to chemists) that silver replaces the whole of the replaceable hydrogen of a hydrogen salt if it replaces any at all, so that the reaction which took place was—

$$3\,Ag\,N\,O_3 + H\,Na_2\,P\,O_4 = Ag_3\,P\,O_4 + 2\,Na\,N\,O_3 + H\,N\,O_3.$$

This hydric nitrate keeps some of the silver phosphate dissolved, so if you wish to convert the whole of a given quantity of a soluble phosphate into the silver salt, you must carefully neutralise the liquid.

295. The formulæ and names of a few of the most important phosphates are here given, chiefly as illustrating the great convenience of the systematic nomenclature lately introduced by Professor Williamson, in indicating the composition of a body by its name.

Formulæ.	Systematic names.	Unsystematic names.
$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}P\,O_4$	trihydric phosphate,	tribasic phosphoric acid.
$\left.\begin{matrix}Na\\H\\H\end{matrix}\right\}P\,O_4$	dihydrosodic phosphate,	acid phosphate of soda.
$\left.\begin{matrix}Na\\Na\\H\end{matrix}\right\}P\,O_4$	hydrodisodic phosphate,	rhombic phosphate of soda. / common phosphate of soda.
$\left.\begin{matrix}Na\\Na\\Na\end{matrix}\right\}P\,O_4$	trisodic phosphate,	subphosphate of soda.

* *I. e.*, regular—those in which the *whole* hydrogen is replaced by the metal.

The potassic and ammonic phosphates have formulæ similar to the sodic ones.

$\left.\begin{matrix}H_2\\H_2\\H_2\end{matrix}\right\}(PO_4)_2$ trihydric phosphate (two molecules).

$\left.\begin{matrix}Ca\\H_2\\H_2\end{matrix}\right\}(PO_4)_2$ tetrahydrocalcic diphosphate { superphosphate of lime.

$\left.\begin{matrix}Ca\\Ca\\H_2\end{matrix}\right\}(PO_4)_2$ dihydrodicalcic diphosphate { bibasic phosphate of lime !

$\left.\begin{matrix}Ca\\Ca\\Ca\end{matrix}\right\}(PO_4)_2$ tricalcic diphosphate, phosphate of lime.

In the case of these compounds of calcium, which is divalent, the first salt must necessarily contain two atoms of phosphorus in the molecule, and also the third salt: the intermediate one might be written $Ca''HPO_4$, but it is unlikely that it is so different in constitution from the others on each side of it. Observe, how a single atom of calcium, by having, as it were, a leg in each of two molecules, serves to bind them together.

Bismuthic phosphate is $Bi'''PO_4$, bismuth being trivalent. Other important phosphates are—$H(NH_4)$, $NaPO_4$, hydro-ammonio-sodic-phosphate, or microcosmic salt, much used in blowpipe analysis; and $(NH_4)_2Mg_2(PO_4)_2$, the so-called ammonio-magnesian phosphate. This last is exceedingly insoluble in water alkaline with ammonia, and is therefore made use of for detecting and estimating soluble phosphates present in a liquid.

296. **Prepare the following reagent and keep it for use. To the solution of half an ounce of magnesic sulphate add ammonia till the solution is strongly alkaline, then add a saturated solution of ammonic chloride, till the precipitate formed by the ammonia is dissolved; add about as much more of the ammonic chloride as was absolutely needed, and filter, if necessary, after the liquid has stood twenty-four hours.**

This alkaline solution of magnesia, if added in sufficient

quantity to an alkaline solution containing a phosphate, precipitates *all* the phosphate present, in the form of a crystalline white precipitate of $Mg_2(NH_4)_2(PO_4)_2$, which adheres to the sides of the glass, especially at those points which have been rubbed with a glass rod. This reaction constitutes a delicate test for the presence of a phosphate in solution.

297. If common phosphate of soda be heated to redness, two molecules lose a molecule of water between them—

$$2\,HNa_2PO_4 - H_2O = Na_4P_2O_7,$$

and leave a salt which is called from its fiery origin "pyrophosphate of soda." If this salt be dissolved in *cold* water it does not again take up this water, and so when nitrate of lead is added there is obtained a precipitate of $Pb_2P_2O_7$, which, if washed, suspended in water, and treated with a current of hydric sulphide, gives $H_4P_2O_7$ and Pb_2S. $H_4P_2O_7$, tetrahydric pyrophosphate or pyrophosphoric acid, and its metallic derivatives, are unimportant. By boiling with aqueous hydric chloride, the hydric pyrophosphate is made to take up the elements of water, and becomes orthohydric phosphate, trihydric phosphate, H_3PO_4.

It may also be remarked that when microcosmic salt, $(NH_4)NaHPO_4$, or di-hydro-sodic phosphate, H_2NaPO_4, are ignited, sodic metaphosphate, $NaPO_3$, is left—water and ammonia escaping in one case, and water alone in the other.

298. There are, therefore, at least three different hydrogen phosphates—

HPO_3,	monohydric phosphate,	or hydric metaphosphate.
$H_4P_2O_7$,		hydric pyrophosphate.
H_3PO_4,	trihydric phosphate,	hydric orthophosphate.

The last two when heated lose water, and give the first; and by boiling either of the first two, the third results from the assimilation of water (the addition of hydric chloride or sulphate greatly facilitates the change).

299. The tests for the presence of the orthophosphates, in the absence of other salts, are :—

In *neutral* solutions they give

With solution of silver nitrate a yellow precipitate of silver phosphate, Ag_3PO_4, soluble both in ammonia and in hydric nitrate.

With baric chloride, $Ba\,Cl_2$, a white precipitate of baric phosphate, $Ba_3\,2\,P\,O_4$, insoluble in ammonia, but soluble in hydric chloride, or nitrate, or acetate.

In *alkaline* solutions they give with an ammoniacal solution of magnesia, a white crystalline precipitate of $Mg_2\,(N\,H_4)_2\,2\,P\,O_4$, soluble in hydric chloride, nitrate, or acetate (acetic acid). This test is available in the presence of any salts (of the alkalies) except the arseniates.

In *acid* solutions, *e. g.*, the solution of bone earth in hydric chloride, they give a bright yellow crystalline precipitate (of uncertain composition) which is soluble in ammonia, when the liquid is boiled with a *large excess* of nitro-molybdate of ammonia. This test is available in the presence of any salts except the arseniates.

The nitro-molybdate of ammonia, which is altogether the best and most delicate test for the phosphates, is prepared by dissolving ¼ oz. "molybdic acid" in a quantity of ammonia only just sufficient, diluting with water to 12 oz., and adding hydric nitrate in large excess, gently warming, setting aside for twelve hours, and filtering.

300. When the product of the slow combustion of phosphorus in a limited supply of air ($P_2\,O_3$) is thrown into water, it forms $H_3\,P\,O_3$, hydric phosphite, or hydrated phosphorous acid, and not $H\,P\,O_2$, corresponding to $H\,N\,O_2$, as would be expected. The same body is produced by exposing moist sticks of phosphorus, each of which is surrounded by a wide glass tube, open at both ends to the air, in a funnel standing in the neck of a bottle. Oxygen and water are absorbed at the same time, and the acid product collects in the bottle. It is best made by throwing phosphorus chloride into water (see § 285), and gently evaporating the liquid till the hydric chloride is expelled. It is a powerful reducing agent, owing to its tendency to become hydric phosph*ate*.

If a solution of hydric phosphite is treated with excess of soda or potash and crystallised, the resulting metallic salt has a composition represented by $Na_2\,H\,P\,O_3$ or $K_2\,H\,P\,O_3$, and it is found impossible to replace the third atom of hydrogen by a metal. Hydric phosphite is, therefore, dibasic only, although it contains three atoms of hydrogen. It is capable of forming but two classes of metallic salts, *e. g.*, $H\,M'\,P\,H\,O_3$ and $M'_2\,P\,H\,O_3$.

When evaporated and heated, it splits up into hydric phosph*ide* and trihydric phosphate—

$$4\,H_3\,P\,O_3 = 3\,H_3\,P\,O_4 + H_2\,P.$$

301. When submitted to the action of nascent hydrogen it yields hydric

phosphide, just as hydric nitr*ite* yields ammonia. A solution of it when boiled with a solution of mercury precipitates the metal in the form of a grey powder, a reaction which renders the detection of any phosphoric trioxide mixed with the pentoxide a matter of great ease.

302. In § 282, a *hypo*phosphite of soda was mentioned as one product of dissolving phosphorus in soda. If we use solution of baric hydrate, $Ba H_2 O_2$, instead of sodic hydrate, Na H O, we obtain $Ba''H_4 P_2 O_2$, or baric hypophosphite; and if we decompose the filtered solution of the salt by the exactly necessary amount of hydric sulphate, we obtain hydric hypophosphite, or "hypophosphorous acid"—

$$Ba H_4 P_2 O_4 + H_2 S O_4 = Ba S O_4 + 2 H_3 P O_2.$$

Only one out of the three atoms of hydrogen in this salt is replaceable by metals. Observe—

$H_3 P O_4$	is	tribasic	That is, that as the proportion of oxygen increases, the basicity also increases. In this sense oxygen is the acid former.
$H_3 P O_3$	is	bibasic	
$H_3 P O_2$	is	monobasic	

303**. Phosphorus and sulphur combine with great violence to form a series of unimportant and not very well defined compounds. The following formulæ have been assigned to them : $P_4 S$, $P_2 S$, $P_2 S_3$, $P_2 S_5$, and $P_2 S_6$. $P_2 S$, $P_2 S_3$, and $P_2 S_5$, are said to unite with alkaline sulphides to form sulphur salts corresponding to the hypophosphites, phosphites, and phosphates.

QUESTIONS ON CHAPTER XII.

1. In what forms does phosphorus occur in nature?

2. In what way does a tiger get the phosphorus necessary for his bones?

3. What is the action of hydric sulphate on "bone ash?"

3 (*a*). What reaction takes place between hydric phosphate and carbon when the two bodies are heated together strongly?

4. Describe the properties of clear phosphorus.

5. Which is the most important "allotropic" modification of phosphorus, and how is it prepared?

6. What is there remarkable about the vapour density of phosphorus?

7. What is the composition of the most important hydride of phosphorus? How is it prepared, and what are its properties?

8. In what way is it analogous to ammonia, besides in its formula? What volume of hydrogen is contained in 10 cc. of it?

9. How is spontaneously inflammable phosphuretted hydrogen prepared? To what does it owe its remarkable power?

10. What volume of air would be required to burn 10 cc. of pure PH_3?

11. If 10 cc. of phosphuretted hydrogen were decomposed into hydric chloride and solid phosphoric chloride (occupying no appreciable volume) by the addition of 50 cc. of chlorine, what volume of gas would remain?—*Ans.* 40 cc.

12. How are the chlorides of phosphorus made?

13. What is the action of water on the tri and penta-chlorides respectively?

14. How is phosphoric pentoxide made? what are its properties? what other name is it known by?

15. What is the *first* action which takes place when phosphoric pentoxide is thrown into water?

16. What occurs when its solution is boiled for a long time, and how is it proved that a new hydrogen salt is formed?

17. How is trihydric phosphate prepared? What are its chief properties?

18. Give the formulæ and names of all the possible potassium and barium salts of trihydric phosphate.

19. How is the presence of a phosphate detected, (*a*) in a neutral liquid, (*b*) in an alkaline one, (*c*) in an acid one?

20. What other hydrogen phosphates are there besides the trihydric one?

21. What is the action of nascent hydrogen on hydric phosphite?

22. What is the formula of hydric hypophosphite? How much of its hydrogen is replaceable by metals?

CHAPTER XIII.

ARSENIC. Symbol As. Atomic weight 75.

Combining vol. $\frac{1}{2}$ or $\boxed{75}$. Molecule = $As_4 = 300$.

304. ARSENIC, which is the third term of the nitrogen group of elements, is mostly found in combination with metals and sulphur, but it is also found in the free state. The metallic arsenides are roasted in furnaces, and the arsenic in them goes off as arsenious trioxide, $As_2 O_3$, which is condensed in long flues. From this oxide of arsenic the element itself can be prepared by the same action as that employed in liberating phosphorus from the "phosphoric acid" obtained from bones, *i. e.*, by heating it with carbon (charcoal).

Put twenty or thirty grains of the "white arsenic" of commerce ($As_2 O_3$) in the sealed end of a two foot length of combustion tube, and fill eight inches of the tube above it with small bits of recently ignited charcoal. Put the tube so prepared into a gas or charcoal tube furnace, and apply heat, first making the *front* part of the charcoal hot, and then extending the fire back to the "arsenic" at the end. As soon as the arsenic oxide gets hot enough it will volatilise, and its vapours in passing over the ignited carbon will part with their oxygen—

$$2\,As_2 O_3 + C_6 = 6\,C\,O + As_4.$$

305. The arsenic, or as it is better called, arsenicum, to avoid confusing it with "white arsenic," will condense on the cold

sides of the tube beyond the charcoal as a dark shining mirror, and the carbonic oxide gas will escape.*

With the arsenicum so prepared, or with a bought specimen, observe that it has a bright surface with a peculiar lustre, a steel-grey colour, and a crystalline structure when freshly broken; that it is of a greater density than any of the other elements we have studied (specific gravity of As = 5·75,) and that it does conduct electricity, though badly. These are properties which those bodies which we call metals possess: and in so far, arsenicum is a metal. Note, the best way of observing the *lustre* of arsenicum is to plunge the specimen into a clear solution of bleaching powder, which dissolves off the grey film on the surface, but does not attack the metal itself at all rapidly.

306. Observe that it is so brittle that it can be easily rubbed to a fine powder; that it does not dissolve in hydric chloride, but does in hydric nitrate (forming As_2O_3 or As_2O_5, according to the strength of the nitrate used). Heat a small quantity in a narrow test tube, it will volatilise *without first melting*, at a temperature of less than 200° Centigrade (*i. e.*, far below a red heat), and will again condense as a crystalline crust of metallic appearance on the cooler parts of the tube. Repeatedly sublime the same portion of arsenic backwards and forwards in a tube full of air, it will become converted into minute brilliant crystals of the trioxide, As_2O_3.

Observe also the peculiar smell (described by some as that of garlic), produced when a *very small* quantity is volatilised in contact with air.

Powder a small quantity, moisten it, and expose it to air; it will become converted into a grey powder owing to partial conversion into As_2O_3.

307. It unites directly with chlorine and iodine at ordinary temperatures, and with sulphur when gently heated. It is said to exist in two allotropic forms, but there is comparatively little known about them.

THE VAPOUR DENSITY of arsenicum is 150; therefore, as in the case of phosphorus, the molecule consists of four atoms.

308. ARSENIURETTED HYDROGEN, ARSENIAMINE, HYDRIC ARSENIDE = $AsH_3 = 78 = 2$ vol., cannot be prepared by the direct

* Perform this and all other experiments with arsenic, especially with arseniuretted hydrogen, in the open air, or in a strong draught.

union of its elements, but is made by one or other of two processes with which we are already acquainted. The one is by dissolving a metallic arsenide in a dilute hydrogen salt, when a reaction analogous to those by which H_2S and H_3P are made takes place (see §§ 146 and 277). The best arsenide to use when pure AsH_3 is wanted is that of zinc, which is to be dissolved in hydric chloride in a flask provided with a chloride of calcium drying tube, &c.

The other, which is less troublesome, gives the gas mixed with free hydrogen, which, however, does not interfere with the observation of its important properties.

Into a small hydrogen apparatus, fitted with a chloride of calcium drying tube, one limb of which contains a small quantity of lead acetate to absorb a possible trace of hydric sulphide, as in fig. 64, and in which hydrogen is being evolved from dilute hydric sulphate by zinc, introduce a small quantity of a solution of arsenic trioxide (As_2O_3). This will lose its oxygen and have it replaced by hydrogen, in the same way that hydric nitrate, or nitrite, or phosphite, are converted into ammonia or phosphamine by nascent hydrogen; only as hydric arsenide is not possessed of the power of combining with acid bodies, it escapes mixed with the excess of hydrogen instead of remaining as a salt in the liquid (comp. § 210),—

$$As_2O_3 + 12\,H = 2\,AsH_3 + 3\,H_2O.$$

Take great precautions to avoid inhaling any trace of this gas, as it is a most deadly poison.

309. Pass the mixed gases, evolved from the apparatus shown in fig. 64, through a quill tube of hard glass, having a drawn-out point, and light them at the end; the flame will be bluish-white, and will give a sort of white smoke of As_2O_3, if the oxidation is complete. Into the flame put a cold porcelain crucible-cover; the combustion will now be only partial, because the temperature is lowered, and the arsenicum will be the portion which remains unburnt; it will therefore deposit on the porcelain as a steel-grey mirror-like spot. After trying the experiment, heat the tube through which the gas is passing to redness, by a lamp. Arsenicum will be deposited on the tube *beyond* (at a greater distance than shown in the fig.), the flame as a mirror-like ring, which can be easily chased about from one part of the tube to another, by a heat far below that at which glass softens.

Observe that arseniuretted hydrogen is decomposed by heat into its elements, like ammonia and phosphuretted hydrogen, only

with more ease. A series of electric sparks also decomposes it as it does ammonia.

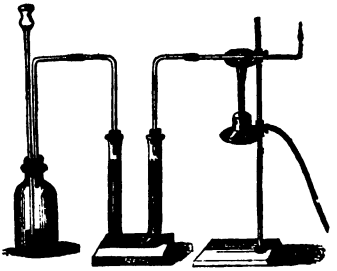


Fig. 64.

310. Any solution of arsenic not containing a nitrate or chlorate yields at least some of its arsenic as AsH_3 when treated in the above manner, even when it is in very small quantity, and mixed with large amounts of other substances. The process, therefore, constitutes a very delicate test for the presence of arsenic compounds, and is known as Marsh's test. The deposit formed on a cold surface is easily volatilised by a gentle heat, is soluble in a solution of bleaching powder, and is converted into hydric arseniate, by warming with hydric nitrate. Perform all the experiments indicated above; the methods of performing them are obvious, and require no explanation.

311. Pass the mixed hydrogen and hydric arsenide from the Marsh's apparatus in slow bubbles through solutions of sulphate of copper and nitrate of silver contained in test tubes. Reactions quite similar to those taking place with hydric phosphide will occur—

$$3\,CuSO_4 + 2\,H_3As = 3\,H_2SO_4 + Cu_3As_2,$$
$$6\,AgNO_3 + 3\,H_2O + H_3As = 6\,HNO_3 + H_3AsO_3 + 3\,Ag_2.$$

In both cases precipitates will be obtained, the one of cupric arsenide and the other of metallic silver. That the arsenic remains in solution in the second case can be shown by precipitating the excess of silver by a solution of hydric chloride, filtering, and adding sulphuretted hydrogen water to the clear liquid, when a yellow precipitate of arsenious sulphide, As_2S_3, will be formed.

312. Arseniamine is, when pure, a colourless gas with a repulsive smell and frightfully poisonous powers, even when much diluted with air. It dissolves in about five times its own volume of water, to which it communicates not the slightest alkaline character. It will not combine even with hydric iodide as phosphamine does, and, indeed, appears to be wholly destitute of basic power.

When phosphorus is heated in arseniamine, it takes up the hydrogen of that body to form phosphamine, and sets the arsenicum at liberty—

$$P_4 + 4\,As\,H_3 = 4\,P\,H_3 + As_4.$$

It has a normal vapour volume, therefore $2 \times 11{\cdot}2$ litres of it, at the normal pressure and temperature, would weigh 78 grammes.

313. Arsenicum is only known to form one chloride, $As\,Cl_3$, which can be made either by burning arsenicum in chlorine, or by distilling together in a retort a mixture of the strongest hydric chloride and arsenic trioxide ($As_2\,O_3$)—

$$As_2\,O_3 + 6\,H\,Cl = 2\,As\,Cl_3 + 3\,H_2\,O.$$

Or better, mix $As_2\,O_3$ with five times its weight of hydric sulphate in a retort, and drop in lumps of fused salt and distil. The oil of vitriol will so thoroughly retain the water formed that a very large product of $As\,Cl_3$ will be obtained.

The retort must be provided with a good condenser, and the distillation must not be pushed too far, or water will come over in too large a quantity. In the receiver will be found two liquids; the lighter one a solution of hydric chloride, which has distilled; and the heavier one the arsenious chloride, in the form of an oily liquid.

314. Arsenious chloride, when thrown into water, is decomposed thus,—

$$2\,As\,Cl_3 + 3\,H_2\,O = As_2\,O_3 + 6\,H\,Cl.$$

But this is exactly the reverse of the reaction by which $As\,Cl_3$

was formed. Now what circumstances are there in the two cases, to explain this apparent contradiction? In the first case there was an *excess of hydric chloride*, and in the second an *excess of water*, though the equations do not show this, because in the end the excess of either remains unchanged. In the first case, the water produced by the reaction of the hydric chloride on one molecule of As_2O_3 is prevented from effecting the opposite change on the $AsCl_3$ produced by being diffused through, and feebly held by, the excess of strong solution of hydric chloride present. In the second case, the excess of water takes up the hydric chloride formed, &c. &c. &c.

315. Observe that the decomposition of arsenic trichloride by water is complete, and that the action is precisely analogous to that between water and phosphoric trichloride; only in this case we obtain the anhydrous body As_2O_3, instead of the corresponding hydrogen salt H_3AsO_3.

$$PCl_3 + 3H_2O = 3HCl + H_3PO_3,$$
$$AsCl_3 + 3H_2O = 3HCl + H_3AsO_3.$$

The second equation doubtless represents the action which first occurs between arsenic trichloride and water; but the hydric arsenite, H_3AsO_3, afterwards splits up into water and "anhydrous arsenious acid"—

$$2H_3AsO_3 = 3H_2O + As_2O_3,$$

as hydric sulphite splits up into water and "anhydrous sulphurous acid," SO_2.

316. The ready formation and volatility of arsenious chloride enables us to separate arsenic from mixtures (*e.g.* the contents of a stomach), in a form fit for examination.

Put a few grains of white arsenic into an ounce or two of soup, evaporate off most of the water at a gentle heat; introduce the residue into a retort, add three or four times its bulk of strong hydrochloric acid, and distill to dryness, into water. Add one portion of the distillate to Marsh's apparatus, and identify the presence of arsenic; treat the other with sulphuretted hydrogen, when a bright yellow precipitate of arsenious sulphide, As_2S_3, will be formed.

317. Arsenic forms compounds with bromine and iodine, $As Br_3$ and $As I_3$, by direct union of the elements. The first is a white, and the second an orange-coloured solid.

The Oxidised Compounds of Arsenic.

318. There are two oxides of arsenicum, $As_2 O_3$, arsenious acid, or arsenic trioxide, and $As_2 O_5$, arsenic acid, or arsenic pentoxide.

$As_2 O_3$ constitutes the "arsenic" or "white arsenic," which is used as a poison. It generally occurs as a white crystalline powder, or as a hard opaline mass, which volatilises at about 200° C. It is slightly soluble in water, with which it does not form any very definite hydrate. When acted on by more powerful bases than water, it gives a series of salts of the formula $M_3 As O_3$, *e.g.* arsenite of silver is $Ag_3 As O_3$; most of them are, however, not very stable, and those of the alkalies are very ill defined.

319. It is very easily reduced to the metallic state by heating in contact with carbon or hydrogen.

Mix a minute portion with a mixture of carbon and carbonate of soda, produced by igniting dry acetate of soda, and heat the mass in a narrow dry tube closed at one end. The soda will unite with the acid oxide and prevent its flying away before the temperature is high enough for the carbon to deprive it of its oxygen. The arsenicum, as it assumes the free state, will sublime and condense on the upper part of the tube.

320. Its aqueous solution is very slightly acid to test paper, and may be considered as consisting of a solution of hydric arsenite, $H_3 As O_3$.

Add dilute ammonia to a solution of silver nitrate, till the precipitate first formed is just, and only just, dissolved, and to this solution of so-called ammonio-nitrate of silver, add an aqueous solution of arsenic trioxide. A bright yellow precipitate of silver arsenite, $Ag_3 As O_3$, will be thrown down, which shows that hydric arsenite is tribasic. Prepare ammonio-sulphate of copper by a method similar to that given for silver, and add the arsenious solution. A bright green precipitate of $Cu_2 As O_3$,

known and used as a pigment under the name of Scheele's Green, will be formed.

NOTE.—Both these precipitates are soluble in hydric nitrate, and also in ammonia.

321. Acidulate some of the solution of "arsenious acid" with hydric chloride, introduce a slip of bright copper foil, and warm the liquid. The copper will become coated with a steel-grey coating of reduced arsenicum. Heat the coated copper in a small dry test tube; part of the arsenicum will sublime off and become oxidised by the air of the tube into As_2O_3, which will condense in small bright crystals in the cool part of the tube. The presence of organic matter does not interfere with this reaction, which is therefore much made use of in "poison cases," under the name of Reinsch's test.

322. Pass sulphuretted hydrogen into a solution of "white arsenic" which has been acidulated with hydric chloride; a bright yellow precipitate of As_2O_3 will be thrown down—

$$As_2O_3 + 3H_2S = 3H_2O + As_2S_3,$$

the arsenic trisulphide will be found to be soluble in ammonia, potash, alkaline sulphides, and alkaline carbonates.

The reactions resulting in the production of the chloride, sulphide, and hydride of arsenicum, together with those giving the silver and copper arsenites, and the production of metallic arsenicum, constitute the tests for arsenic.

323. Like hydric phosphite, hydric arsenite (or arsenic trioxide in solution) is possessed of reducing powers. By mere exposure to air it slowly becomes hydric arseniate, H_3AsO_4. When boiled with a solution of gold it precipitates that metal.

The vapour density of arsenic trioxide is very anomalous; it is 198, *i.e.* is equal to its molecular weight ($As_2 = 150$; $O_3 = 48$ ∴ $As_2O_3 = 198$), instead of $\frac{198}{2}$, as it should be according to theory.

324. When metallic arsenic, or its trioxide, is boiled with strong hydric nitrate, it is converted into an acid hydrogen salt, which, after neutralisation with potash or ammonia, gives a brick-red precipitate with silver nitrate. The precipitate has a composition represented by Ag_3AsO_4; therefore the hydrogen salt from which it is derived is H_3AsO_4, analogous in its com-

position, mode of preparation, and (as will be presently shown) properties to H_3PO_4.

Boil together, in a small basin, a quarter of an ounce of arsenic trioxide and a quantity of strong hydric nitrate, more than sufficient to cover it. When action has ceased, add more of the nitrate, and heat again, and continue these operations as long as the evolution of red fumes gives evidence of the reduction of the hydric nitrate. Evaporate off the nitrate used in excess, and heat a portion of the resulting mass to *very* dull redness over a lamp, in a place where fumes will be carried away (*e.g.* on the hob of a fire-place, having a fire in it to create a draught).

A white amorphous mass of As_2O_5 will be left. It is very slightly soluble in water. The portion which has not been ignited will yield crystals of trihydric arseniate, if dissolved in water, evaporated to a syrupy liquid, and allowed to stand for a long time.

325. Without going to the trouble of crystallising the solution of trihydric arseniate, neutralise some with sodic carbonate, and crystallise. You will obtain $HNa_2AsO_4 + 12H_2O$, or hydrodisodic arseniate, which has all the appearance and crystalline form of the corresponding phosphate (rhombic or common phosphate of soda). By treating this phosphate with caustic soda, or with hydric arseniate (H_3AsO_4), and crystallising, you can obtain salts corresponding to the other orthophosphates, Na_3AsO_4 and NaH_2AsO_4.

326. An alkaline solution of an arseniate gives, with an ammoniacal solution of magnesia, a precipitate $(NH_4)_2Mg_2(AsO_4)_2$ which, like the corresponding phosphate, is very insoluble in alkaline liquids; with silver nitrate it gives a characteristic brick-red precipitate of silver arseniate, Ag_3AsO_4. Arseniates are so much like phosphates, that they can only be distinguished from them by the ease with which they are reduced,* and by these reduced solutions giving AsH_3, when introduced into an apparatus evolving hydrogen, and a yellow precipitate of As_2S_3, when treated with sulphuretted hydrogen. Nitro-molybdate of ammonia (§ 299) behaves with a solution of an arseniate just as it does with a phosphate. No compounds of arsenic corresponding to HPO_2 and $H_4P_2O_7$ are known with any certainty.

Trihydric arseniate is an oxidising agent. Boil its solu-

* An arseniate is reduced to an arsenite when boiled with a solution of hydric sulphite.

tion with one of hydric sulphite, and prove that the latter has been converted into hydric sulphate.

327. Arsenic forms three compounds with sulphur, As_2S_2, realgar or red orpiment, As_2S_3, arsenic trisulphide or sulpharsenious acid, yellow orpiment, and As_2S_5 (?), arsenic pentasulphide, or sulpharsenic acid.

The first is prepared by melting the two elements together. The second by passing hydric sulphide into an acid solution of arsenic trioxide, when it is precipitated as a bright yellow powder, insoluble in hydrochloric acid, but soluble in alkalies, alkaline carbonates, and alkaline sulphides—

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O.$$

It forms sulphur salts by combining with many metallic sulphides, *e.g.* Ag As S_3, silver sulpharsenite. The third sulphide, As_2S_5, has probably never been obtained in the free state, but when As_2S_3 is dissolved in an alkaline sulphide, and boiled with sulphur, a sulpharseniate is formed by a reaction, which is analogous to the conversion of a phosph*ite* into a phosph*ate* by oxidation.

QUESTIONS ON CHAPTER XIII.

1. How is metallic arsenic or arsenicum prepared?
2. How many grammes would 100 litres of arsenicum vapour weigh at a temperature at which the same volume of hydrogen weighed 4 grammes?
3. Describe the appearance and properties of arsenicum?
4. How can arsenicum be converted into its trioxide?
5. By what reactions can arseniuretted hydrogen be prepared?
6. What weight of arsenicum is contained in a litre of As H_3?
7. What volume of air would be required to completely burn 1 litre of pure arseniamine?—*Ans.* 7·5 litres of pure air.
8. How can metallic arsenic be obtained from hydric arsenide?
9. What reaction shows that arsenicum combines with hydrogen less forcibly than phosphorus does?

10. How is arsenic trichloride prepared? How is it decomposed by water?

11. If a mass of organic matter, say the contents of a stomach, was suspected to contain arsenic, how would you proceed to obtain any "arsenic" present in a state fit for "testing?"

12. What is "white arsenic," and how is it obtained?

13. How would you prove the presence of "arsenious acid" in a watery solution?

14. Describe Reinsch's test for arsenic.

15. What is the action of sulphuretted hydrogen on an acidified solution of "arsenic?"

16. How can arsenic pentoxide or "anhydrous arsenic acid" be made?

17. Compare the effect of evaporating and heating solutions of trihydric arseniate and the corresponding phosphate.

18. How can an arseniate be distinguished from a phosphate?

CHAPTER XIV.

ANTIMONY. Symbol Sb. Atomic weight 120.

328. THE fourth term of the nitrogen series of elements occurs for the most part as a sulphide, Sb_2S_3, which is the body known in commerce as "antimony," but it is also found native in small quantities, and as an oxide. The metal, which, is called "regulus of antimony," is obtained from this sulphide by either of the two following processes :—

Mix powdered sulphide of antimony with a little less iron, in the form of filings or turnings, than is required to remove the sulphur according to the equation

$$Sb_2S_3 + Fe_3 = 3FeS + Sb_2,$$

add to the mixture a little common salt, put the whole into an earthenware crucible capable of holding twice as much, and set the crucible in a fire where it can be raised to bright redness. Put a cover on the crucible, and heat slowly at first. The iron will take the sulphur as shown by the equation, and when the heat is sufficient, the ferrous sulphide formed will melt, as well as the antimony, and being lighter than that body will float on its surface. The salt is added to facilitate the *flowing* of the melting mass, and is therefore called a flux. Remove the crucible from the fire and allow it to become quite cold ; then break it with a hammer and remove the button of antimony.

The other method is to roast (*i.e.* heat strongly in a current of air) the sulphide till most of the sulphur is burnt away and replaced by oxygen ; and then to heat the resulting oxide, Sb_2O_3, with carbon (charcoal) and carbonate of soda in a crucible.

$$Sb_2O_3 + C_3 = Sb_2 + 3CO.$$

329. Antimony possesses those properties which we call metallic even in a higher degree than arsenic, *e.g.* its lustre is higher, its Sp. Gr. (= 6·7) is greater, and it conducts heat and electricity better. Again, it unites with metals, such as copper, lead, and silver, to form *alloys*, *i.e.* compounds, in which the metallic properties of the constituents are not lost. It melts at 430° C., and slowly volatilises at a bright red heat, *i.e.* at a point above the melting point of glass; it is hard, crystalline, and easily powdered. At ordinary temperatures it does not oxidise in the air, but at a red heat it rapidly forms Sb_2O_3. As shown in § 78, it unites readily with chlorine. When very finely powdered, it dissolves slowly in strong-boiling hydric chloride solution. The action of hydric nitrate on it is very energetic, as can be shown by pouring some on the powdered metal, which will thereby be converted into a white powder, consisting of an oxide of the metal,—pentoxide, if the nitrate is very strong. *Strong boiling hydric sulphate converts it into antimonic sulphate*, with evolution of sulphuric dioxide. "Aqua regia" converts it into trichloride.

Antimony is much used for rendering other metals hard, *e.g.* type metal is lead hardened by antimony.

330. Antimonuretted Hydrogen, Hydric Antimonide, stibiamine, SbH_3 = 123 = 2 vol. The compound of antimony with hydrogen has never been obtained in a pure state; its composition might, therefore, be open to doubt. It is obtained, mixed with free hydrogen, by introducing a solution of chloride of antimony into a "Marsh's apparatus," or, better, by dissolving an alloy of 1 part antimony and 10 parts zinc in dilute hydric sulphate.

331. It is a colourless, inodorous gas, insoluble in water, and totally devoid of basic power. When passed into a solution of silver nitrate, it forms a black precipitate, which analysis shows to be $SbAg_3$; now silver is monovalent, therefore the reaction must have consisted in replacing the hydrogen of the antimonu-

retted hydrogen by silver, and the reaction which occurs between the two must be

$$3\,Ag\,N\,O_3 + Sb\,H_3 = 3\,H\,N\,O_3 + Sb\,Ag_3,$$

which is analogous to the reaction between hydric sulphide and silver nitrate,

$$2\,Ag\,N\,O_3 + S\,H_2 = 2\,H\,N\,O_3 + S\,Ag_2,$$

so removing all doubt as to the composition of antimonuretted hydrogen. It burns with a bluish-white flame, which gives *black* spots of antimony on any cold object plunged into it. It is decomposed, by being passed through a red-hot tube, even more readily than the hydride of arsenic; indeed, it decomposes at a temperature below redness, and gives rings of metallic antimony on both sides of the flame which heats the tube. These reactions might cause antimony and arsenic to be mistaken one for the other; but the antimony rings in the tube cannot be volatilised by the heat of a lamp (compare § 309), and the spots which the flame forms on porcelain are not dissolved by a solution of bleaching powder, whereas those of arsenic are.

332. Collect some mixed hydrogen and antimonuretted hydrogen in a tube full of mercury, and pass up into the gas a strong solution of cupric sulphate. The whole of the antimony compound will be absorbed (being converted into $Cu_3\,Sb_2$) while the free hydrogen will be left. In this way the amount of each present in the original gas can be estimated. Repeat the experiment with the arsenic and phosphorous compounds of hydrogen.

333. Antimony forms two chlorides; $Sb\,Cl_3$, antimoni*ous* chloride or antimonic trichloride, corresponding to phosphoric and arsenic trichlorides; and $Sb\,Cl_5$, antimonic chloride or antimonic pentachloride, corresponding to phosphoric pentachloride.

Fix a three foot length of combustion tube in the neck of a tubulated receiver by means of a collar of india-rubber tube. Fill it with fragments of metallic antimony, after contracting the end which enters the receiver; connect the tubulus of the receiver with an apparatus for furnishing dry chlorine. Set up a current of gas. The metal will unite rapidly, and with great evolution of heat, with the chlorine, first to form the trichloride, which will then unite with more chlorine to give the penta-

chloride, which will flow back into the receiver in the form of an oily yellow liquid. Put aside some of the pentachloride in a bottle, the stopper of which has been well smeared with melted paraffin.

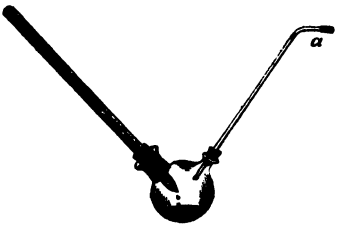


Fig. 65.

Powder the metal which remains in the tube, or a fresh portion; put it in a retort and pour on it the remainder of the pentachloride. Distil (a rather high temperature will be required). The metal will react on the pentachloride thus,

$$3\,SbCl_5 + Sb_2 = 5\,SbCl_3,$$

forming the trichloride, which will condense in the receiving flask (or wide test tubes, which are better), as a brittle-white crystalline mass—known in an impure form as "butter of antimony."

334. Or, the trichloride can be made by dissolving the sulphide, or oxide, of antimony in boiling concentrated solution of hydric chloride.

$$Sb_2S_3 + 6\,HCl = 2\,SbCl_3 + 3\,H_2S$$
$$Sb_2O_3 + 6\,HCl = 2\,SbCl_3 + 3\,H_2O.$$

The liquid so obtained is a solution of $SbCl_3$ in hydric chloride; it is to be cautiously evaporated to about half its bulk in a basin, introduced into a retort, together with some coarsely-powdered metallic antimony to prevent "bumping," and then distilled till the distillate begins to solidify in the neck of the retort. The receiver is then to be changed, and the chloride collected. By exposing this solid chloride to chlorine in excess, it takes up another two atoms, and forms $SbCl_5$. But these two last atoms of chlorine are held so feebly, that merely boiling the liquid suffices to expel them (compare § 284).

335. Throw some of the terchloride into a moderate excess of water. A thick white precipitate of Sb O Cl, antimon*ious* oxichloride, will be

formed; wash this for a long time with hot water; it will lose all its chlorine and give Sb_2O_3. The two reactions are

$$SbCl_3 + H_2O = SbOCl + 2HCl$$
$$2SbClO + H_2O = Sb_2O_3 + 2HCl.$$

Add aqueous hydric chloride to the liquid containing the precipitate formed by water with the terchloride; the whole will become clear, even if much water be present; but if to this clear liquid you add a large quantity of water, the precipitate will be again produced.

Compare these statements carefully with § 314, and explain the reactions here given by the light of that paragraph.

Notice that the decomposition of the chloride by water is not so complete as in the cases of phosphorus and arsenic.

336. The pentachloride of antimony loses two atoms of chlorine when boiled, and would therefore give a four volume vapour, like the corresponding compound of phosphorus, if an attempt were made to take its vapour density.

When thrown into excess of water it gives a white precipitate, which is doubtless trihydric antimoniate, formed by a reaction similar to that which gives trihydric phosphate when phosphoric chloride is similarly treated.

With a small quantity of water it forms crystals, which are probably antimonic oxychloride, $SbOCl_3$.

337. There are three oxides of antimony—

Sb_2O_3	Antimonic teroxide, corresponding to . .	N_2O_3, P_2O_3, and As_2O_3,
Sb_2O_4	Antimonic tetroxide, corresponding to . .	N_2O_4, ? ?
Sb_2O_5	Antimonic pentoxide, or anhydrous antimonic acid, corresponding to . .	N_2O_5, P_2O_5, and As_2O_5.

Antimonic teroxide can best be made by boiling the antimonious oxichloride, SbClO (§ 335), with carbonate of soda,

$$2SbClO + Na_2CO_3 = 2NaCl + CO_2 + Sb_2O_3,$$

and washing and drying the yellowish white powder so obtained. The points about it which are most interesting are, that it possesses *no acid character; e.g.* forms no definite compounds with potash or soda, but, on the contrary, acts as a very weak base, *e.g.* it reacts with hydric sulphate to form a sulphate; and that it combines directly with oxygen to form Sb_2O_4, when heated in the air. Make the experiment, and remark that its analogue, N_2O_3, also unites with oxygen to form N_2O_4.

Prepare the trioxide, wash and dry it thoroughly, weigh off a gramme or two in a weighed porcelain crucible, and ignite by a lamp. It will burn like tinder. Allow the crucible and its contents to cool, and weigh again. The increase of weight will show how much oxygen has combined with it.

338. The antimony salts, formed by dissolving Sb_2O_3 in hydric salts (hydrated acids), are all decomposed by excess of water with production of white insoluble basic salts, unless a body like hydric tartrate or hydric citrate (tartaric or citric acid) be present. Hydric sulphide gives an orange-coloured precipitate of Sb_2S_3 in these solutions, even when very dilute. Confirm these statements with a solution of the trichloride in dilute hydric chloride. Further, observe that if a weak solution of the antimony compound be boiled with metallic copper, that metal becomes covered with a purple coating, which cannot be sublimed off by heat. Tin throws down the whole of the antimony from an acid solution of the trioxide as a black powder.

339. Antimonic tetroxide, Sb_2O_4, made as before described in § 337, or by igniting the product of the action of hydric nitrate on the metal, is a yellowish white powder, which is slightly soluble in water.

340. Antimonic pentoxide, Sb_2O_5, is a yellowish powder, made by gently heating monohydric antimoniate, $HSbO_3$. When ignited it loses an atom of oxygen and becomes Sb_2O_4, as N_2O_5 becomes N_2O_4. It is insoluble in water, and does not react with that body to form hydric salts.

When antimonic pentachloride is acted on by water in excess, a precipitate of the composition H_3SbO_4 is thrown down by a

reaction analogous to that occurring when phosphoric pentachloride is similarly treated.

$$Sb\,Cl_5 + 4\,H_2O = Sb\,O_4\,H_3 + 5\,H\,Cl.$$

Trihydric antimoniate is very unstable, losing one molecule of water with the greatest ease, and becoming $H\,Sb\,O_3$.

The product of the action of hydric nitrate on antimony is monohydric antimoniate, $H\,Sb\,O_3$, the analogue of hydric nitrate, $H\,N\,O_3$, and monohydric phosphate, $H\,P\,O_3$. It is a yellowish powder, which, when moist, turns litmus paper red; it dissolves in potash solution to form $K\,Sb\,O_3$.

The salts corresponding to $H\,Sb\,O_3$ are the most stable of all the antimoniates; they are mostly insoluble.

When the potassium salt $K\,Sb\,O_3$, produced by igniting $Sb_2\,O_5$ with potassic carbonate, is evaporated with excess of potassic hydrate, it becomes $K_4\,Sb_2\,O_7$ (generally called potassic metantimoniate), analogous to $K_4\,P_2\,O_7$, potassic pyrophosphate (§ 297).

The soda salt corresponding to this, viz. $Na_4\,Sb_2\,O_7$, is very insoluble.

341. There are two sulphides of antimony, $Sb_2\,S_3$ and $Sb_2\,S_5$. The first is found native as a crystalline lead-grey mass, and is formed as an orange precipitate when hydric sulphide is passed into any acid solution of antimony corresponding to the trioxide. The second is made by passing the same gas through a solution of pentachloride of antimony in tartaric acid. It is orange-yellow.

Both sulphides dissolve in boiling hydric chloride. Both are sulphur acids, and therefore dissolve in alkaline sulphides to form sulphur salts. The sulph-antimon*ites* are of rather indefinite composition, but the sulph-antimoni*ates* have a composition represented by $M_3\,Sb\,S_4$. The soda salt crystallises in peculiarly fine tetrahedrons.

Antimony is not known to form any compound with nitrogen.

The reactions which characterise antimony compounds, or in other words, the tests for antimony are,—

1° The production of stibiamine SbH_3, when the soluble ones are acted on by nascent hydrogen in acid solutions. The ready decomposition of this gas by heat with formation of a non-volatile metallic crust, not dissolved by solution of bleaching powder.

2° The production of a white precipitate when added in *concentrated* solutions to water (in absence of tartarates, &c.).

3°. The formation of an orange-coloured precipitate of sulphide when their acid solutions are treated with hydric sulphide, which precipitate is soluble in alkaline sulphides and in potash, but not in ammonic carbonate.

4°. By the ready reduction of a brittle bead of metal from all of them when mixed with sodic carbonate and heated on charcoal in the inner flame of the blowpipe.

NOTE—These reactions are decisive of the presence of antimony, only if they are *all* exhibited by the same solution.

QUESTIONS ON CHAPTER XIV.

1. Which is the commonest ore of antimony?
2. How is metallic antimony prepared from it?
3. What are alloys? What is type metal?
4. What is the action of strong hot hydric sulphate on antimony?
5. How is antimonuretted hydrogen prepared?
6. What proof is there that it has the composition assigned to it?
7. How is it distinguished from the corresponding arsenic compound.
8. What compounds does antimony form with chlorine? How are they prepared, and what is the action of water on them?
9. What oxides of antimony are known, and what bodies do they correspond to?
10. What is the action of heat (in presence of air) on the tri and pent-oxides?
11. Which are the most stable antimoniates?
12. What are the tests for antimony?

CHAPTER XV.

BISMUTH. Symbol Bi. Atomic weight 210.

342. THIS metal, which is the fifth and last term of the nitrogen series, is found mostly in the metallic state, but it also occurs as sulphide. The metal is separated from the earthy bodies (quartz principally) accompanying it by simple fusion—the ore is heated, and the metal which runs out as it melts is collected.

It is a reddish-white metal, hard, highly crystalline, and consequently brittle. Beautiful crystals of bismuth can be made by melting a pound or two in a ladle, allowing it to cool slowly, piercing the crust which forms on the surface, and pouring out the still fluid portion. On breaking the shell of bismuth so formed, it will be found lined with beautiful iridescent crystals of a very obtuse rhomboidal form.

343. Bismuth melts at 267° C., and boils at a white heat. Like arsenic and antimony it is hardly acted on by hydric chloride, but is converted into its sulphate by boiling with strong hydric sulphate. Hydric nitrate attacks it readily, and converts it into its nitrate, Bi $(N O_3)_3$.

At a red heat it rapidly combines with the oxygen of the air, and it unites with chlorine, iodine, and sulphur with great ease.

It unites very readily with other metals to form alloys, which are characterised by great fusibility. An alloy of one atom each of bismuth, tin, and lead constitutes *fusible metal*, which melts below the boiling point of water. The specific gravity of bismuth is 9·9.

344. Bismuth is not known to form any compound with hydrogen.

345. Bismuthic trichloride, $Bi Cl_3$. This, the only known chloride of bismuth, is prepared,

1st, by the direct union of the two elements; 2ndly, by dissolving bismuthic oxide, $Bi_2 O_3$, in hydric chloride, evaporating off the water and excess of hydric chloride, and distilling the residue; and 3rdly, by dissolving bismuth in "aqua regia," and treating the acid solution of bismuthic chloride as in 2.

It is a fusible, volatile, granular solid, of a greyish white colour. It deliquesces in the air, and dissolves in a small quantity of water *without decomposition*. By a large quantity of water it is decomposed like the corresponding compound of antimony, *i. e.*, it exchanges two-thirds of its chlorine for an equivalent quantity of oxygen.

$$Bi Cl_3 + H_2 O = Bi O Cl + 2 H Cl.$$

346. The oxychloride of bismuth so formed is a white insoluble powder, which retains its chlorine with so much force that it cannot be removed by washing with any amount of water. It is to be observed that, the hydric chloride formed in the above reaction retains a portion of the bismuth in solution, in the same way as in the corresponding cases of antimony and arsenic chlorides, it prevents the total decomposition of those bodies by the water; and, indeed, owing to the greater stability of the bismuth chloride, it prevents the decomposition of even a larger quantity of the latter by a given quantity of water.

347. The bromide of bismuth, $Bi Br_3$, is formed by dissolving powdered bismuth in bromine; it is decomposed by water in the same way as the chloride.

The iodide is prepared by adding a solution of potassic iodide to a solution of bismuthic chloride or nitrate in acetic acid. It separates as a brownish precipitate, which is decomposed by boiling water, with formation of Bi O I.

348. Only two oxides of bismuth are known with certainty; Bi_2O_3, bismuthic trioxide, and Bi_2O_5, bismuthic pentoxide, or anhydrous bismuthic acid. Another oxide, said to have the composition, Bi_2O_4, has also been described. Bismuthic trioxide is formed, when the metal is strongly heated in the air or oxygen, as a yellow crystalline powder; also when the nitrate of bismuth is ignited, or when the hydrate is boiled in a concentrated solution of potassic hydrate.

It is a yellow fusible solid, which loses its oxygen very readily when heated with carbon or hydrogen, and reacts with most hydrogen salts to form the corresponding bismuth compounds, *e.g.*,

$$Bi_2O_3 + 6HCl = 2BiCl_3 + 3H_2O$$
$$Bi_2O_3 + 6HNO_3 = 2Bi(NO_3)_3 + 3H_2O$$
$$Bi_2O_3 + 3H_2SO_4 = Bi_2(SO_4)_3 + 3H_2O.$$

349. When a solution of one of these salts is precipitated with potash or soda, a hydrate of bismuth is formed, which bears the same relation to the teroxide that hydric nitrite does to nitric teroxide,

$$Bi(NO_3)_3 + 3HKO = HBiO_2 + 3KNO_3 + H_2O,$$

but bismuthous hydrate, $HBiO_2$, is wholly devoid of acid properties, and acts entirely as a basic hydrate, *i. e.*, it reacts with hydric salts, such as hydric nitrate or sulphate, to form bismuth salts.

350. Bismuthic pentoxide is prepared by heating hydric bismuthate, $HBiO_3$, to 130° C. It is a brown powder, which decomposes when strongly heated,

$$Bi_2O_5 = Bi_2O_3 + O_2.$$

When heated with hydric chloride it causes an evolution of chlorine,

$$Bi_2O_5 + 10HCl = 2BiCl_3 + 5H_2O + 2Cl_2.$$

351. Hydric bismuthate, $H\,Bi\,O_3$, the bismuth analogue of $H\,N\,O_3$, $H\,P\,O_3$, and $H\,Sb\,O_3$, is made by suspending bismuthous hydrate in a strong solution of potassic hydrate, boiling the liquid, and passing chlorine gas through the mixture. It is a red body, possessed of feeble acid characters. The oxidising action of chlorine in this case is probably due to the formation of potassic hypochlorite, $K\,Cl\,O$, which readily parts with its oxygen.

352. Bismuth forms two compounds with sulphur; $Bi_2\,S_2$, corresponding to orpiment, and $Bi_2\,S_3$, bismuthic trisulphide. The latter is formed as a brownish black precipitate when hydric sulphide is passed through the solution of a bismuth salt. It is not soluble in alkaline sulphides, and therefore appears not to be possessed of acid properties, any more than its oxygen analogue, $Sb_2\,O_3$.

353. Bismuth differs from all the elements hitherto studied in forming a series of salts by replacing hydrogen in hydric salts.

Bismuthic nitrate, $Bi\,(N\,O_3)_3$, is made by dissolving the metal or its oxide in hot hydric nitrate and crystallising, is a white salt which crystallises easily, and is decomposed by water, with formation of a body insoluble in water—the so-called basic nitrate of bismuth, which, however, is soluble in hydric nitrate.

Bismuthic sulphate, $Bi_2\,(S\,O_4)_3$, is made by dissolving the metal in concentrated hydric sulphate. It is decomposed by water with separation of a basic salt, *i. e.*, a salt in which there is an excess of the basylous constituent.

The other salts of bismuth are mostly insoluble white powders, prepared by precipitating a solution of the nitrate by a solution of a corresponding potash or soda salt, *e. g.*, the phosphate,

$$Bi\,(N\,O_3)_3 + Na_2\,H\,P\,O_4 = Bi\,P\,O_4 + 2\,Na\,N\,O_3 + H\,N\,O_3.$$

354. The tests for bismuth are,

Its solutions, when freed from excess of acid hydrogen salts by evaporation, give white precipitates of basic salts on addition of water. These

precipitates are soluble in hydric chloride. Hydric sulphide gives a brownish-black precipitate of Bi_2S_3 in bismuth solutions. The precipitate is not soluble in alkaline sulphides.

Metallic zinc throws down all the bismuth present in the form of black or grey powder of metallic bismuth. Potash, or soda, throws down bismuthous hydrate as a white precipitate insoluble in excess of the precipitant.

CHAPTER XVI.

355. COMPARISON of nitrogen, phosphorus, arsenic, antimony, and bismuth.

In this series of elements we observe that as the atomic weights increase, the physical states or forms of the members alter in the same way as in the chlorine and oxygen groups, thus,

Nitrogen, atomic weight, 14, is a gas at all temperatures.

Phosphorus, „ „ 31, is a solid at ordinary temperatures, a liquid at 45° C., and a gas at 290° C. It is quite devoid of metallic characters, and has a specific gravity of about 2.

Arsenic, „ „ 75, is solid at all temperatures below 180° C., and has feebly marked metallic characters, and a specific gravity 5·6.

Antimony „ „ 120, is solid below 450° C., and only boils at a white heat. Is very metallic in appearance and properties, and has a specific gravity 6·7

Bismuth „ „ 210, does not melt below 267° C., and boils at a white heat. Is a very perfect metal, with a specific gravity of 9·9.

356. The hydrogen compounds of the elements of this series likewise differ much as those of the other two series differ.

Ammonia is decomposed with great difficulty by heat, and is capable of uniting with acid bodies with great readiness.

Phosphamine is decomposed by heat, with more facility than ammonia, and exhibits less basic power.

Arseniamine is easily decomposed by heat, and is devoid of basic power.

Stibiamine is formed with difficulty, and decomposes completely below a red heat; it has no basic power.

Compare these statements with regard to the stability of the compounds with those made about water, hydric sulphide, hydric selenide and telluride, hydric chloride, bromide, and iodide.

357. In their oxygen compounds we also observe that as the atomic weights increase, the stability likewise increases, though not in a marked manner after the two first terms. The oxides of phosphorus are much more stable than those of nitrogen, but not perceptibly less so than those of the remaining members.

The oxides containing three or five atoms of oxygen are in the cases of nitrogen and phosphorus strongly acid, and give well defined salts by the action of water or metallic oxides. In the case of arsenic the trioxide is feebly acid in character, but its pentoxide rivals that of phosphorus. Antimony trioxide is almost entirely devoid of acid characters, and, indeed, acts as a weak base, witness its sulphate. Antimony pentoxide is acid, and forms salts which are not, however, either very stable or well defined. Lastly, bismuth trioxide is strongly and decidedly basic in character, while the pentoxide even is but very feebly acid.

QUESTIONS ON CHAPTERS XV. AND XVI.

1. In what forms is bismuth found? How is it extracted?

2. What actions have hydric chloride, nitrate and sulphate, respectively on bismuth?

3. What is the chief characteristic of bismuth alloys?

4. How is chloride of bismuth made? Compare the action of water on it with that of the same body on the corresponding compounds of phosphorus, arsenic, and antimony.

5. How is bismuthic trioxide prepared?

6. What is the action of a solution of potash or soda on one of bismuthic nitrate or chloride?

7. How does the hydric derivative of bismuthic teroxide differ from the corresponding compounds of nitrogen, phosphorus, and arsenic?

8. Which term of the nitrogen group first exhibits a basic character in its teroxide?

9. Which are the most, and which the least, stable compounds of hydrogen with the members of the chlorine, oxygen, and nitrogen groups respectively? Quote experiments which demonstrate the truth of your statements.

CHAPTER XVII.

ELEMENTS WHICH ARE GENERALLY TETRAVALENT.

CARBON, SILICON, AND TIN.*

CARBON, Symbol C. Atomic weight 12. Volume unknown.

358. Is one of the most abundant elements in nature, and occurs both free and combined. The native forms of free carbon are diamond and plumbago. The diamond is too well known to need description; its density is 3·5; it is the hardest body known; it does not conduct electricity; and crystallises in forms belonging to the cubical system (1st system). It is the purest form of carbon. Plumbago, graphite, or black lead, when of the best quality, is almost as pure as diamond; its density is variable; it is very soft, as is shown by its use in "lead pencils;" it has a feeble metallic lustre; it conducts electricity well, and crystallises in hexagonal tables belonging to the rhomboidal system (3rd system). Carbon is, therefore, dimorphous, like sulphur (§ 142). These two dense forms of carbon burn with great difficulty.

359. The substances which contain carbon in a combined form are exceedingly numerous, including all animal and vegetable substances, without exception, the "air" (as CO_2), "waters" (in the same form), and a great variety of minerals, such as chalk, limestone, &c., which occur in enormous masses.

360. It is always prepared artificially from organic bodies (*i. e.*, bodies *derived* from things having "organs" adapted to

* In addition to these there are Titanium and Zirconium, which are very rare, and not much studied.

special purposes, such as plants which have leaves, roots, &c). All organic substances contain carbon and hydrogen, most contain oxygen as well, and a great many contain nitrogen. All these elements, with the exception of carbon, are volatile; therefore, when an organic body is strongly heated, they go off in various forms of combination, carrying some carbon with them, but leaving a great part of that element behind in most cases.

Heat some bits of wood to redness in a covered crucible, you will have "charcoal" left. This operation is performed on a large scale either by heating the wood in large iron retorts by a

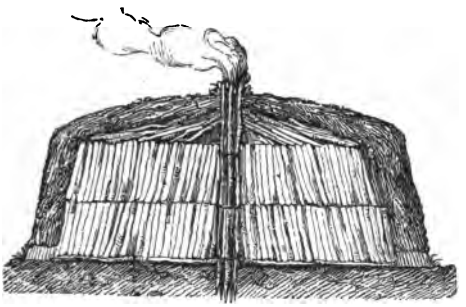


Fig. 66.

separate fire, or by charring one portion of wood by the slow combustion of another. In the last case the wood is built up into a great mound round a central shaft, covered with earth, and fired from the middle. The combustion is then regulated by admitting more or less air through small openings made in the earthen cover. When "tar" ceases to be formed, all openings are closed, and the mound left to cool for a fortnight. The charcoal is then removed.

361. Charcoal varies very much in density, according to the wood from which it is made. The denser varieties, such as that from boxwood, conduct electricity, the slighter ones, such as that from willow wood, do not. They all burn in air or oxygen with ease. Charcoal is exceedingly porous, and possesses a remarkable power of absorbing gases.

Nearly fill a tube with dry ammonia, or hydrochloric acid gas, over mercury; then heat a bean-sized bit of compact charcoal to redness to expel air and moisture; while still glowing, plunge it beneath the surface of the mercury, and after the lapse of a few seconds, allow it to ascend into the gas in the tube. Observe that the volume of the gas rapidly diminishes. Any gas might be used, but the more soluble ones are more largely absorbed than the others.

1 vol.	of	boxwood	charcoal	absorbs	90	vol. ammonia,
,,	,,	,,	,,	85	,,	hydric chloride,
,,	,,	,,	,,	55	,,	hydric sulphide,
,,	,,	,,	,,	9·25	,,	oxygen,
,,	,,	,,	,,	1·25	,,	hydrogen,

at the ordinary atmospheric temperature and pressure.

362. This property of charcoal is most valuable, since it constitutes it a powerful deodoriser and disinfectant. Exposed to air contaminated with putrescent organic matter, it absorbs the particles which cause the smell and those which communicate disease, and at the same time oxygen from the air. The gases absorbed by the charcoal must necessarily be in a very condensed state, and, therefore, are more capable of acting one on the other; accordingly, the organic portions are burnt by the oxygen and destroyed.

Crush an ounce or so of fresh wood charcoal, put it in a small flask, bury the bulb of a thermometer in it (or the bulb of the thermoscope shown on p. 98, if the experiment is to be shown to a class), insert the delivery-tube of an apparatus for evolving hydric sulphide into the flask, put a little cotton wool round the tube and the stem of the thermometer so as to prevent draughts interfering, and set up a current of the hydric sulphide.

Fig. 67.

Immediately a considerable rise of temperature will manifest itself, owing to the hydric sulphide being burnt by the condensed oxygen in the pores of the charcoal. The rise of temperature will cease as soon as the oxygen in the charcoal is all consumed. Keep up the current of gas till the charcoal has returned to its original temperature (or within

a few degrees of it), and then turn out the charcoal, which is now saturated with hydric sulphide, into a beaker glass, and plunge the thermometer again into it.

A rise of temperature greater than in the first case will occur, and all smell of hydric sulphide will disappear, owing to the same action as before taking place to a greater extent, because hydric sulphide is absorbed in large quantity by the charcoal, and is then burnt by the oxygen, which is now in unlimited quantity, and can be continually renewed in the pores of the charcoal.

Bury a bit of putrid flesh in a box of fresh charcoal, taking care that it is surrounded on all sides. No foul smell will be perceived.

363. Coal is vegetable matter which has already undergone a considerable amount of carbonisation. If the carbonisation be completed by one of the methods given for charcoal, "coke" is produced. Coke contains more mineral matter than charcoal; it is denser, and not so porous, and so does not absorb gases in the same way.

364. The product of heating bones in closed vessels is generally called animal charcoal. It is, of course, only a mixture of carbon with tricalcic phosphate (§ 295), the carbon being derived from the destruction of the gelatine of the bones. This variety of carbon is very porous, and, therefore, absorbs gases pretty readily, but its chief importance lies in the fact that it is capable of absorbing vegetable colouring matters from solutions.

Boil together in a flask a solution of sulphate of indigo, and an ounce or two of animal charcoal in coarse powder. Filter, and observe that the original deep blue liquid has become colourless. This property is much made use of for decolorising yellow solutions of raw sugar in the process of refining.

As wood, coal, and bones all contain mineral matter which is non-volatile, the carbon obtained from them is impure. Pure varieties of artificial carbon can only be made by charring things, such as pure sugar, which contain no mineral constituents, or by getting it from gases by burning them incompletely.

365. Lampblack, which is very pure carbon, after it has

been strongly heated, was first obtained by catching the soot from a lamp. It is made on a large scale by burning resinous and fatty refuse of various kinds in an insufficient supply of air, and passing the dense smoke so produced through long horizontal flues, where the lampblack settles. It is used as the basis of all black paints, and is the foundation of printers' ink.

366. Carbon unites directly with oxygen and sulphur, as will be shown shortly, but not with chlorine, iodine, nitrogen, phosphorus, &c. &c.

When strongly heated, it is a very powerful reducing agent, as can be shown by—

Heating together in a crucible a mixture of plumbic oxide, Pb O (litharge), and lampblack, or powdered charcoal. Metallic lead will be obtained,

$$2\,Pb\,O + C_2 = Pb_2 + 2\,C\,O.$$

Cupric oxide, or, indeed, the oxide of almost any element, may be substituted for the lead oxide with similar results if a sufficiently high temperature be employed. Even water vapour, when passed over strongly ignited carbon in a tube, yields hydrogen and carbonic oxide.

COMPOUNDS OF CARBON WITH HYDROGEN.

367. The compounds of carbon and hydrogen are excessively numerous, amounting, indeed, to many hundreds. The study of most of them belongs to organic chemistry, which has been called the chemistry of carbon.

That compound which contains most hydrogen in proportion to carbon, and which, therefore, fixes the atomicity of the latter, is

$C\,H_4 = 16 = 2$ vol. MARSH GAS, LIGHT CARBURETTED HYDROGEN, FIRE DAMP.

It has received the first name, because it was originally

obtained from a stagnant pool in a marsh. If a bottle has a funnel loosely fitted in its mouth, and is then filled with water in a pool having black mud at the bottom, and inverted over a spot in the mud which is being stirred with a stick, the gas which is entangled in the mud will rise and pass into the bottle. It will be found to be combustible. It is derived from the decay of vegetable matter.

The name fire damp is obtained from its being found in coal pits, where it too often catches fire, and (when mixed with air) produces explosions.

It is called *light* carburetted hydrogen, because it is the lightest gas known next to hydrogen itself. (Calculate its density as compared with hydrogen and as compared with air.)

Its systematic name is methylic hydride.

It is always produced when organic substances are submitted to destructive distillation at a high temperature.

368. To prepare it artificially, the best plan is to mix dried acetate of soda ($NaC_2H_3O_2$) with an excess of caustic soda, and as much lime as will prevent the mixture fusing,* and then to heat the mixture strongly in a florence flask or small retort coated with clay (see Appendix), the reaction which takes place is represented by

$$\underbrace{NaC_2H_3O_2}_{\text{sodic acetate.}} + NaHO = CH_4 + \underbrace{Na_2CO_3}_{\text{sodic carbonate.}},$$

The gas can be collected in the ordinary manner over water, or can be burnt from the end of the tube after passing through a cold empty bottle. It burns with a pale yellowish flame, which gives hardly any light; but if passed through a tube heated to bright redness, it afterwards burns with a much brighter flame. The igniting point of marsh gas is very high; it requires to be raised to a temperature at which iron is in a state of *bright* redness, before it will burn in air. Its lightness, insolubility in water, want of odour, colour, &c., can be proved

* Good proportions are, 1 part of dried acetate of soda, and 3 parts of ordinary "soda lime" (a ready-made mixture of soda and lime, which can be bought).

by experiments which readily suggest themselves. It is an exceedingly inert gas, and seems incapable of uniting directly with anything.

369. That it really contains four atoms of hydrogen united to one of carbon weighing 12, and not one of hydrogen united to one of carbon weighing 3, or two of hydrogen and one of carbon weighing 6, which would all, of course, give the same results on analysis, is shown by the action of chlorine on it. If marsh gas be mixed with its own volume of chlorine, and if the mixture be then exposed to sunlight, a reaction takes place, hydric chloride is formed, and at the same time a body which can be condensed by cold into a liquid having the composition $C H_3 Cl$, (C = 12); now, the reaction must have been

$$C H_4 + Cl_2 = C H_3 Cl + H Cl.$$

That is, *one-fourth* of the hydrogen has been replaced by chlorine, and therefore there must have been four atoms; the reasoning being parallel to that in the cases of water (§ 56), and ammonia (§ 213). Further, by repeating the action of chlorine in sunlight, we can replace successively the remaining atoms of hydrogen, and so from

$C H_4$	hydride of methyl, get in succession,
$C H_3 Cl$	chloride of methyl,
$C H_2 Cl_2$	dichloride of methylene,
$C H Cl_3$	chloroform,
$C Cl_4$	tetrachloride of carbon.

370. When it is burnt, water and carbonic dioxide are formed:

$$C H_4 + O_4 = C O_2 + 2 H_2 O.$$

But $C H_4$ = 2 vol., and O_4 = 4 vol.; therefore marsh gas requires twice its own volume of oxygen to burn it completely. Further, the carbonic dioxide ($C O_2$) formed being a two-vol. gas, its bulk is equal to that of the marsh gas burnt. If the combustion of a given volume of marsh gas were effected at a

temperature above that at which water condenses, the products of combustion would occupy three times the space of the marsh gas burnt, or the same space as the mixed marsh gas and oxygen (all being measured at the same temperature and pressure).

As air only contains $\frac{20{\cdot}8}{100}$ of its volume of oxygen, as much more air than oxygen is required as $\frac{100}{20{\cdot}8}$: 1; so that to burn 1 vol. of marsh gas completely, we need $2 \times \frac{100}{20{\cdot}8}$ vol. of air; or, in round numbers, five times as much air as pure oxygen.

371. It may be mentioned that marsh gas is the first term of a series of hydrocarbons, the members of which all contain CH_2 more than the next lower member. They extend from CH_4, marsh gas, up to a limit not yet fixed, but are known to include one containing $C_{27}H_{56}$, one kind of paraffin. Series of bodies, the members of which are analogous in constitution, and vary by CH_2, or multiples of that quantity, are called homologous series.

372. The other compound of carbon and hydrogen which we will study is olefiant gas, heavy carburetted hydrogen, or ethylene, C_2H_4.

It is one product of the destructive distillation of organic bodies when the temperature employed is not excessive. When passed through a strongly ignited tube it deposits carbon.

For the purposes of experiment, it is best made by heating in a flask a mixture of one part of strong alcohol, and four parts of concentrated oil of vitriol. The hydric sulphate abstracts the elements of water from the alcohol (C_2H_6O),

$$C_2H_6O + (H_2SO_4)_n = C_2H_4 + (H_2SO_4)_n, H_2O.$$

In performing the experiment, mix enough coarse dry sand with the contents of the flask to convert them into a thick mud, or towards the end of the operation there will be a very inconvenient amount of frothing.

Pass the gas evolved through two wash bottles, one containing pumice and soda, and the other pumice and oil of vitriol. The first will absorb carbonic dioxide and sulphuric dioxide produced by a secondary

reaction, and the other will take up vapour of alcohol and ether. Collect the gas in the "bottle gas-holder," and perform the following experiments. 1st. Burn some from a jet, and notice that it gives a

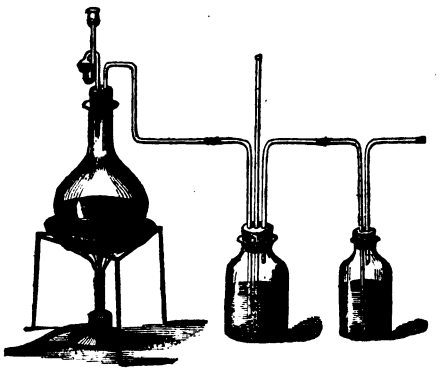


Fig. 68.

bright smoky flame. 2nd. Fill up with it a bottle which is rather less than half-full of chlorine. In a short time the colour of the chlorine will disappear, and oily drops will collect on the sides of the bottle. Whence the name olefiant (oil-producing). This oil, which is called "Dutch liquid," and dichloride of ethylene, has a formula of $C_2H_4Cl_2$; it has a normal vapour volume (2 vol.), and a smell like that of chloroform.

372 (*a*). Carbon forms several chlorides, the two most important being CCl_4, made as above described, or by the action of antimonic pentachloride on carbonic disulphide,

$$CS_2 + 2\,SbCl_5 = 2\,SbCl_3 + S_2 + CCl_4.$$

It is a thin, colourless oil, which boils at 77° C.; it is very soluble, but is decomposed at a red heat into chlorine, and a number of other chlorides, such as C_2Cl_6, C_2Cl_4, and C_2Cl_2.

373. Olefiant gas, like marsh gas, is the first term of a homologous series of hydrocarbons. They all contain twice as many atoms of hydrogen as carbon, C_2H_4, C_3H_6 —, C_nH_{2n}, and therefore give the same results on analysis. That C_4H_8, for

example, is not the same body as C_2H_4 is proved by the fact that the density of its vapour is twice as great as that of olefiant gas at the same temperature, and that therefore its molecule contains twice as many atoms. Also its compound with chlorine contains a quantity of chlorine which shows it to be $C_4H_8Cl_2$. Bromine may be substituted for chlorine in the experiment given above, and with advantage, as it is easy to prepare some quantity of ethylenic dibromide, by simply passing olefiant gas into a flask containing an ounce or two of bromine just covered with water, and shaking while the supply of the ethylene is continued, till the bromine has lost all colour and become converted into a heavy oily body. The boiling point of ethylenic dibromide is higher than that of the chloride.

374. Carbon unites directly with oxygen at high temperatures to form either CO, carbonic oxide, or CO_2, carbonic dioxide, according to the proportions of the two elements present.

Carbonic Dioxide, or Carbonic Acid Gas,*

$$CO_2 = 44 = 2 \text{ vol.},$$

can be prepared by burning carbon or one of its combustible compounds in excess of oxygen or air, but as it is practically impossible to cause carbon to combine with the whole of any given quantity of oxygen without causing some of the lower oxide to be also formed, this method is not applicable to the preparation of the pure gas, since the product will always contain either some carbonic oxide, or an excess of oxygen.

375. When any metallic carbonate is acted on by a strongly acid hydrogen salt, its metal is replaced by hydrogen in the usual way, but instead of hydric carbonate, there is obtained water and carbonic dioxide arising from its decomposition, *e. g.*,

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2CO_3,$$

* The name "carbonic acid" will be often used in the following pages instead of the more systematic one "carbonic dioxide," because, like the name "salt," as applied to sodic chloride, it is almost a household word.

but H_2CO_3 splits up thus, $H_2CO_3 = H_2O + CO_2$, just as sulphuric dioxide and water result from the decomposition of a sulphite by a hydrogen salt.

Put some small lumps of marble, chalk, limestone, or other convenient carbonate, into the apparatus used for preparing hydrogen, cover them

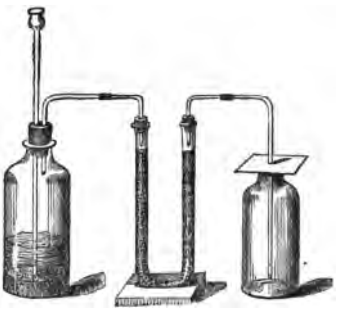


Fig. 69.

with water, and add commercial "muriatic acid" * slowly. A brisk effervescence is immediately set up, and a gas comes off, which can be collected by downward displacement.

Marble, chalk, and limestone are more or less pure forms of native calcic carbonate, $CaCO_3$, and when this is acted on by the hydric chloride, the changes described above take place, the whole reaction being represented by

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

Any carbonate and any "strong acid" may be used, *e. g.*,

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2,$$
$$KHCO_3 + HNO_3 = KNO_3 + H_2O + CO_2,$$
$$BaCO_3 + 2HClO_3 = Ba2ClO_3 + H_2O + CO_2.$$

376. Prove that carbonic acid is heavier than air by pouring it downwards through air from one vessel into another containing a burning

* Hydric sulphate might be used, only calcic sulphate is so slightly soluble that the apparatus becomes choked with it.

taper, which will be extinguished. Also by leaving a wide-mouth bottle of the gas open with the mouth upwards for some minutes, and another with the mouth downwards for the same time, and then testing each with a lighted taper on a wire. The light will be extinguished in the first case and not in the second.

Fill a very large beaker, or other cylindrical jar, with the gas, and prove that it is full by lowering a burning taper gently into it. Then take a smaller beaker and *dip out* some of the gas, and see that you have done so by proving that the level of the gas in the big jar is lower, and that the small beaker is filled with gas. Blow a soap bubble which will sink in air, and allow it to fall on the surface of the remaining gas, it will float as if on water; or, if the jar is big enough, you may let a child's air ball (one of those very thin india-rubber ones) float on the gas.

377. Prove that carbonic acid is soluble in water, and that the solution has a faint acid reaction, capable of turning litmus to a wine-red colour; and further observe that this reddening is not permanent, but disappears when the paper is exposed to air.

At ordinary temperatures and pressures, water is capable of absorbing its own vol. of this gas. If the gas be subjected to pressure, its volumes decreases. (The vol. of a gas is inversely as the pressure, *i. e.*, if a gas be subjected to a pressure 2, 3, 4 . . . . n times as great as the atmospheric pressure, its vol. becomes $\frac{1}{2}, \frac{1}{3}, \frac{1}{4} \ldots \frac{1}{n}$ times its original vol.). But still water dissolves its own bulk of this compressed gas. If water which contains this condensed gas be relieved from the pressure on its surface, all the gas which is dissolved over and above the normal quantity escapes with violence, producing effervescence. Soda-water, champagne, &c., owe their sparkling properties to this circumstance. Many other gases behave in the same way; indeed, nearly all which are not very soluble in water.

378. Carbonic acid gas is one of those which can be liquefied by cold and pressure. At ordinary temperatures a pressure of from 35 to 40 atmospheres is required to reduce it to the liquid form, and therefore the vessel in which it is condensed must be of great strength. The best and safest way of condensing it is to force it into a wrought-iron receiver by a powerful force pump constructed for the purpose; but it is often liquefied by its own pressure. In the latter case it is generated in a strong iron cylinder by the action of somewhat dilute oil of vitriol on bicarbonate of soda. As it is evolved it of course exerts a continually increasing pressure

on the vessel and on itself until the pressure reaches about 35 to 40 atmospheres, according to the temperature, when it begins to condense and the pressure becomes constant. This first cylinder is then put in communication with a second furnished with a tube passing to the bottom. The first cylinder is gently warmed while the second is surrounded by ice. The condensed gas distils out of one into the other, and then when all is supposed to have passed over, the cock of the second vessel is closed and the two separated. If the cock of the vessel containing the condensed gas be opened, the pressure which its vapour exerts (35 to 40 atmospheres) forces the liquid up the tube and out of the opening into the air. Being now relieved of the pressure which kept it liquid a part suddenly evaporates, and in so doing absorbs so much heat that the remainder (of that which has left the vessel) freezes into a snow-like powder, which can be caught in a suitable brass box. This solid carbonic dioxide evaporates very slowly, and may be handled with impunity if not pressed, because it is as it were bedded in an atmosphere of gas which it is always giving off, and gases are almost incapable of conducting heat, which is accordingly abstracted from the fingers but slowly. A mixture of this solid carbonic dioxide with ether evaporates very rapidly in the air, and still more rapidly in the air pump vacuum, and thereby produces a cold of —100° C., which suffices to condense many gases and to freeze most liquids, except alcohol. The intense cold of this mixture causes wounds similar to burns if it be applied to the skin.

379. The solution of CO_2 may be considered to contain H_2CO_3, just as the solution of SO_2 contains H_2SO_3, and as SO_2 reacts with basic oxides and hydrates to form sulphites, so does CO_2 combine to form carbonates, M'_2CO_3 or $M''CO_3$.

Fill a long narrow tube with the gas, and invert it in a solution of sodic or potassic hydrate. The liquid will rapidly rise in the tube, showing that the gas is absorbed.

$$2KHO + CO_2 = K_2CO_3 + H_2O.$$

If we pass carbonic dioxide into a solution of caustic soda in a flask, it is rapidly absorbed,

$$CO_2 + 2NaHO = Na_2CO_3 + H_2O,$$

and disodic carbonate is formed; but if now we continue to pass the gas and to agitate till the liquid is quite saturated,* we obtain hydro-

* Known by the thumb not being sucked inwards when the liquid is shaken up with the gas collected in the upper part of the flask.

sodic carbonate, as, under parallel circumstances, we obtain hydrosodic sulphite,

$$Na_2CO_3 + H_2OCO_2 = 2HNaCO_3.$$

The normal carbonates of potassium, sodium, and ammonium, &c., are very strongly alkaline, and even those which are acid in *constitution*, *e.g.* $NaHCO_3$ and $KHCO_3$, are alkaline in reaction, because "carbonic acid" is not strongly acid enough to neutralize such powerfully alkaline bodies as potash and soda. All the carbonates, except those of the alkalies, are insoluble, and may therefore be prepared by precipitation, *e.g.*,

$$BaCl_2 + K_2CO_3 = BaCO_3 + 2KCl.$$

The formulæ and names of a few carbonates are given a little further on; those marked * are mostly found in union either with the oxide or hydrate of the metal.

380. Pass carbonic acid gas slowly into a glass of somewhat diluted lime water. The first bubbles will render the liquid troubled, and the turbidity will go on increasing with the succeeding bubbles up to a certain point, and then the liquid will begin to grow clear again. When all the precipitate has redissolved, and the liquid is quite transparent, boil some of it in a large test tube for several minutes. The precipitate will reappear.

Now to explain this. The first action was a simple union of the dissolved lime, CaO, with the gas, CO_2, so we had $CaCO_3$ formed, which, being insoluble in water, precipitated, and caused the cloudiness. The subsequent excess of carbonic acid caused this precipitate to dissolve, but when the liquid was boiled, this excess was expelled, and the calcic carbonate, having nothing to dissolve it, again fell. This is a very important property of carbonic acid, for as the air contains carbonic acid, and as rain, in falling through it, absorbs some of it, and as the solution so made soaks through strata containing calcic carbonate and then emerges in the form of springs, spring water always has carbonate of lime in solution, and when boiled deposits it in the form of a crust on the sides of the boiler. Moreover, this semi-free carbonic acid escapes from the solution by simple exposure to the air, and the calcic carbonate which it holds in solution is, therefore, slowly deposited. Examples of this can be seen under most stone or brick bridges. The rain water charged with carbonic acid in filtering through the mortar

takes up calcic carbonate, and afterwards deposits it in the form of miniature stalactites as it drips from the lower surface of the arch. The stalactites in caverns are formed in the same way.

381. To detect the presence of carbonic dioxide, it is only necessary to shake up any gas suspected to contain it with an excess of clear lime water, when a cloudiness will immediately show itself if any be present. "Baryta water" may be substituted with advantage for lime water, if small quantities have to be detected.

Lower a candle into a large dry bottle of air, and allow it to stay there till it goes out for lack of oxygen. Observe the sides of the bottle are bedewed with moisture, and that therefore the material of the candle contained hydrogen. Then pour in some lime water and shake; a precipitate will be formed showing the presence of carbonic acid, and therefore of carbon in the candle. In the same way you may prove that "coal gas," wood, and most other ordinary combustibles, contain these two elements, carbon and hydrogen.

List of some important carbonates:

382. $Na_2CO_3 + 10H_2O$ (di)sodic carbonate, "soda," washing soda.

$NaHCO_3$ . . hydrosodic carbonate, bicarbonate of soda.

K_2CO_3 . . . (di)potassic carbonate, "potashes," pearl ash.

$KHCO_3$ . . hydropotassic carbonate, bicarbonate of potash.

$NaKCO_3 + 6H_2O$ sodio-potassic carbonate, double carbonate of potash and soda.

$(NH_4)_2CO_3$ (?). (di) ammonic carbonate,

$(NH_4)HCO_3$. hydro-ammonic carbonate; } mixture of the two, smelling salts.

$CaCO_3$ . . . calcic carbonate, Iceland spar, marble, chalk, &c.

$BaCO_3$ . . . baric carbonate, Witherite.

*$ZnCO_3$ . . . zinc carbonate.

*$CuCO_3$ . . . cupric carbonate.

The last occurs only as so-called basic carbonates, *e.g.*, in the mineral "malachite."

383. A modified process of slow combustion takes place in the bodies of animals when they respire; consequently our breath contains carbonic acid. Prove it by expiring through a bit of tube into some lime water.

Fermentation and decay give rise to the production of this same gas, which accordingly collects in disused wells, brewers' vats, &c., and often occasions fatal accidents to persons entering them.

Make a mixture of one part brown sugar, ten parts warm water, and a little yeast in a flask; fermentation will begin in a short time, and carbonic dioxide will come off rapidly, and may be passed through a tube into lime water. At the same time the sugar is converted into alcohol.

384. Air containing any considerable quantity (2 per cent.) is very injurious to animal life, consequently unventilated rooms having many people in them are unhealthy. The quantity of carbonic dioxide yearly poured into the atmosphere is enormous: no reliable estimate can be made of its amount, but some idea may be formed of its vastness, thus:—About 174,000,000 tons of coal are burnt every year. This coal contains on an average 60 per cent. of carbon, that is, 104,400,000 tons of carbon. Each 12 tons of carbon forms 44 tons carbonic dioxide, therefore from this source alone we have 382,800,000 tons of carbonic dioxide yearly. Probably as much more is made by the burning of other fuels, and then to that we must add all which is expired by all the animals in the world, and again to all this a vast amount due to decay of vegetable matter, and again that which is belched forth by volcanoes.

What becomes of all this burnt carbon? It evidently has not been collecting in the air for ages, for the air only contains 0·04 per cent. of it. Let us consider a smaller thing than the whole world, at first; a small portion of "life" placed under conditions which are easily observed and regulated, and then apply what we there observe to explain the greater. Fish placed in a globe of water soon die if the water is not changed, because they, like

all other animals, take up free oxygen, and give out carbonic acid; so that in a short time all the *dissolved free* oxygen in the water is used up, and carbonic acid takes its place; they cannot live without free oxygen, or with carbonic acid. In what is called an "aquarium" fish live an indefinite time without change of water. What is the difference between the two cases? The aquarium contains *growing plants.* When the sun is shining on the aquarium, we may observe a number of little strings of gas bells ascending from different parts of the healthy plants, and if we collect some of the gas in a narrow test tube full of water, and examine it, we find it to be almost pure oxygen. Here, then, is a source of the free oxygen which the fish, &c., require, but the question then remains, from what do the plants elaborate the oxygen?—they evidently can't make it. As the fish continue to live, and as they cannot do so if there be much carbonic acid present, at any rate unless there be a *great* excess of free oxygen present at the same time, the carbonic acid which they are continually producing must be as continually in course of being destroyed, and in the case given there appears to be nothing to do this except the plants. Make a direct experiment to see if plants have the power thus to break up carbonic acid.

385. Pass carbonic acid gas through water for some time, so as to get a solution of the gas. Put this solution in a deep glass basin or large beaker; sink in it a bunch of fresh "parsley," cover this with a short-necked funnel, and stand over the funnel a test tube filled with water. Nothing will visibly occur so long as the whole is not exposed to sunlight; but when the direct rays of the sun fall on the green leaves, oxygen will be given off from the latter, and will pass up into the test tube, in a state of sufficient purity to relight a glowing splint.

Plants, then, under the influence of sunlight, *unburn* carbonic acid, keeping its carbon, and setting free, at any rate, some of its oxygen. The consequences of this power of plants are enormous. Apart from the purification of air and water already mentioned, they include the existence of vegetable life, and, therefore, of food and fuel. The soil often contains no appreciable

amount of carbon, and seldom such an amount as bears any reasonable proportion to that which the crops (trees, &c), raised from it ultimately contain. Therefore, as the carbon cannot be *made*, it must come from the decomposition of the carbonic acid of the air.

It is not known how plants effect this unburning of carbon; but it is known that they are able to do so only under the influence of sunlight.

386. The experiment which is now to be described is of great importance, but unfortunately is somewhat difficult of performance. It establishes the composition of carbonic dioxide, and serves at the same time to determine the atomic weight of carbon.

Its principle is to burn a known weight of carbon, and to weigh the carbonic dioxide produced. These operations are performed by help of the apparatus shown in the fig.

The gas holder contains oxygen which can be forced out through the exit tube by the pressure of water contained in (*a*), through a wash bottle containing oil of vitriol, a U tube containing caustic potash in lumps to absorb any carbonic acid or chlorine which may be in the oxygen, and finally through another U tube (omitted in cut) of pumice soaked in oil of vitriol to thoroughly dry the gas. The tube in the sheet iron furnace is a 30 in. length of combustion tube containing a column of porous oxide of copper 15 in. in length in the end furthest removed from the oxygen (it must not come within four inches of the cork). To use this arrangement, weigh carefully a small porcelain boat with about 0·3 gramme of some tolerably pure and quite dry form of carbon in it. (Diamond, strongly ignited lampblack, or better, the charcoal made by igniting white sugar very strongly.) Place this boat with its contents in the tube at the end next the oxygen supply, leaving at least three inches between it and the oxide of copper; then bring the oxide of copper *alone* to a dull red heat, and pass a little oxygen over it to drive out every trace of moisture. Fill a small U tube, having limbs of about four inches in length, with fresh "soda lime," from which the dust has been removed by sifting; fit it with india-rubber corks and connecting tubes in the usual way, allow it to cool, weigh it, and attach it to the end of the combustion tube in a thoroughly air-tight manner. Heat that part of the tube containing the boat (the oxide of copper being kept red-hot), while a gentle stream of oxygen is kept up. The carbon will burn into carbonic dioxide, which will

pass on through the oxide of copper,* and into the tube of soda lime (not shown in cut), where it will be absorbed. When all the carbon ap-

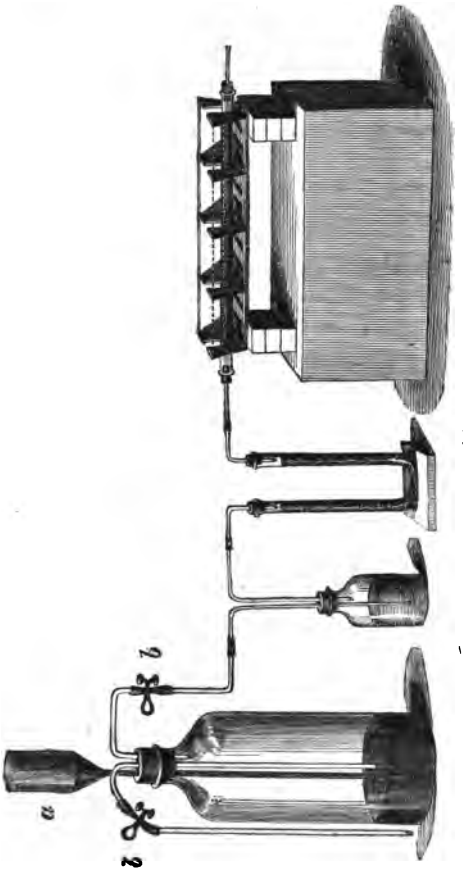


Fig. 70.

pears to be burnt, allow the whole to cool, while a stream of oxygen is still kept up to drive on the carbonic dioxide in the tube, and weigh the

* Which is used to *ensure* the conversion of any CO which *might* be formed into CO_2.

boat again; its loss of weight shows how much carbon has actually been burnt. Weigh the soda lime tube; its gain is the weight of carbonic dioxide formed.

387. Suppose the weight of carbon burnt was 0·33 gramme, and the weight of carbonic acid formed to be 1·21 gramme, then 1·21 gramme of this carbonic dioxide contains ·33 gramme carbon, and ·88 gramme of oxygen, or in one hundred parts

$$\text{Carbon} = 27{\cdot}27$$
$$\text{Oxygen} = 72{\cdot}73.$$

But how do we obtain the formula $C O_2$ from these numbers? Even admitting that the atomic weight of carbon is 12, and that of oxygen 16, 27·27 per cent. of carbon means 27·27 units of carbon out of 100 units of carbonic acid, and so with the 72·73 per cent. oxygen. But we want to know, not how many units of oxygen there are as compared to the units of carbon (or *vice versa*), but how many atoms of one as compared with the other. Now, if in 100 parts of carbonic acid there be 27·27 parts of carbon, there can only be $\frac{27{\cdot}27}{12}$ atoms of carbon, and $\frac{72{\cdot}73}{16}$ atoms of oxygen; that is, in 100 parts of carbonic acid there are

$$\left\{\begin{array}{l}\text{Carbon, } 2{\cdot}273 \text{ atoms, and}\\ \text{Oxygen, } 4{\cdot}545 \quad ,,\end{array}\right.$$

Taking the least of these numbers as unity, and finding the simplest numbers which will express the same ratio, we find that $2{\cdot}273 : 4{\cdot}545 :: 1 : 2$; therefore, carbonic acid consists of one atom of carbon united with two atoms of oxygen (admitting O = 16, and C = 12), and its formula must be $C O_2$.

388. Now, suppose we had wanted to determine the atomic weight of carbon. Taking the same numbers for the purposes of an example, we find that 1·21 gramme of carbonic acid contains ·88 gramme oxygen, and ·33 gramme carbon. But

if ·88 gramme of oxygen unites with ·33 gramme carbon, 16 parts of oxygen (the admitted atomic weight of oxygen) must unite with 6 parts of carbon, for ·88 : ·33 :: 16 : 6.

If, now, carbonic acid was the only compound of carbon and oxygen, and we had no other evidence of the atomic weight of carbon than that afforded by its oxygen compound, we should conclude that carbonic acid was correctly represented by CO, in which $C = 6$, and $O = 16$. But there is another oxide of carbon which only contains half as much oxygen; therefore carbonic acid must contain at least two atoms of oxygen and $O_2 = 32$, and the quantity of carbon united to this weight is shown by experiment to be 12 parts, whence the atomic weight of carbon = 12, unless we can obtain evidence that the carbon in carbonic acid is divisible, which we cannot.

Moreover, two volumes of carbonic acid gas contain 12 parts by weight of carbon, *e. g.*, 11·2 × 2 litres of it contain 12 grammes of carbon, or 44·4 × 2 cubic inches contain 12 grains (the volumes of the gases being, of course, taken at the normal pressure and temperature).

389. The formulæ assigned to chemical bodies are obtained by a method similar to that used in the case of carbonic acid, and are not the result of guess work. To take an example in full. A salt of unknown composition was submitted to examination.

It was crystallised and soluble, alkaline in reaction; it effervesced with acid bodies, giving off carbonic acid. It was therefore an alkaline carbonate. By qualitative tests it was proved to contain both potassium and sodium.

0·55 gramme was dissolved by hydric chloride solution in an apparatus which admitted of the evolved carbonic acid being completely collected in a weighed soda lime tube. The weight of carbonic acid obtained was ·1054 gramme, which is equal to ·1435 gramme of CO_3. The acid solution remaining from this operation was mixed with excess of platinic tetrachloride, and evaporated to dryness, and the mass exhausted (*i. e.* rendered free from soluble matter) with alcohol, and the remaining yellow precipitate of K_2PtCl_6 collected on a filter, dried, and weighed; it weighed ·5835 gramme, and therefore contained ·0932 gramme of potassium.

The solution filtered from the last precipitate was mixed with hydric sulphate, evaporated to dryness and ignited; by this the platinic chloride present was completely decomposed (metallic platinum being left),

and all sodium present converted into its sulphate. The ignited mass was exhausted with water, and the solution so made was evaporated to dryness and ignited in a weighed basin. ·1721 gramme of sodic sulphate was thus obtained, and then it was found by calculation that the sodium in that salt equalled ·0553 gramme.

Lastly, a fresh quantity of ·675 gramme of the original salt was weighed off in a tared platinum crucible, dried and ignited; the loss of weight (due to escape of water of crystallisation) = ·3169 gramme.

∴ ·55 grm.	gave	·1435 grms.	CO_3,	100 grms. would give	26·09
,,	,,	·0932 grms.	K,	,, ,,	16·94
,,	,,	·0553 grms.	Na	,, ,,	10·05
∴ ·675	,,	·2582 grms.	Aq	,, ,,	46·94
					100·02

Then $\frac{26·09}{60^*} = ·4349$ atoms CO_3

$\frac{16·94}{39^*} = ·4346$,, K,

$\frac{10·05}{23^*} = ·4370$,, Na,

$\frac{46·94}{18^*} = 2·6077$,, H_2O.

It is evident that the first three are present in equal numbers of atoms within the limits of experimental error, and that the water is to, say the potassium, as 6 : 1.

Therefore there was found to be in this salt,

One atom each of potassium and sodium, united with such a quantity of carbon and oxygen as is represented by CO_3, and a quantity of water represented by $6H_2O$, and its formula accordingly was,

$$KNaCO_3, 6H_2O.$$

390. As carbonic acid is such a very important body, it may be advisable to summarise its properties.

It is a colourless, invisible gas, 22 times as heavy as hydrogen, and $\frac{22}{14·4}$ times as heavy as air. It has a faint, pungent smell

* $CO_3 = 60$, $K = 39$, $Na = 23$, $H_2O = 18$.

and taste, slight acid reaction when moist, is soluble in its own volume of water, is somewhat poisonous, and incapable of supporting the combustion of most bodies.* It combines with basic oxides, and forms the carbonates, which constitute a large class of very important minerals. It is decomposed by growing plants under the influence of sunlight.

Carbonic Oxide, $CO = 28 = 2$ vol.

391. Made 1st. by burning carbon in an insufficient supply of air, 2nd. by reducing dry carbonic dioxide by passing it through a long tube containing fragments of charcoal or iron turnings at a bright red heat,

$$CO_2 + C = 2CO,$$
$$4CO_2 + 3Fe = 4CO + Fe_3O_4.$$

A three-feet length of half-inch iron gas pipe, being filled for two feet of its middle with charcoal or iron, will serve well. The gas, as it issues from the end of the tube, must be passed through a bottle filled with pumice soaked in a strong solution of caustic soda, to absorb that portion of carbonic dioxide which always remains unreduced. Collect the gas in the bottle gas-holder.

392. Another method gives the gas with less trouble, but is somewhat dangerous in the hands of a beginner. It is to heat oxalic acid, with concentrated oil of vitriol, in a flask, and to pass the resulting gas through a bottle of pumice stone and caustic soda (an apparatus like that shown on p. 66, only of smaller size, is the best). Oxalic acid is $C_2H_2O_4$, and

* Potassium burns in it, as can be seen by filling a dry florence flask with dry carbonic dioxide, dropping in a piece of potassium, loosely closing the mouth of the flask by a plug of cotton wool, and heating the metal till it burns. Potassic oxide will be formed, and carbon, in the form of a black powder, deposited on the sides of the flask—

$$CO_2 + K_2 = K_2O_2 + C.$$

The *molecular* weight of carbon is unknown.

when heated with oil of vitriol it splits up into water and a mixture of carbonic oxide and carbonic dioxide,

$$H_2C_2O_4 + (H_2SO_4)_n = CO + CO_2 + (H_2SO_4)_n H_2O.$$

393. Carbonic oxide is colourless, insoluble in water, incondensable, *very poisonous*, does not support combustion, but burns with a bright blue flame, producing carbonic dioxide,

$$2CO + O_2 = 2CO_2.$$

It is a powerful reducing agent, as may be shown by passing it over ignited oxide of lead.

Carbonic oxide is a very anomalous body; the quantity of it which occupies 2 vol., and which is, therefore, its molecular weight, contains one atom of a tetravalent element, and one of a divalent one; the molecule, therefore, contains two unsatisfied powers of combination, and acts like a free diatomic element in uniting directly with other diatomic elements or molecules. As for instance, when it unites with oxygen (O″) to form CO_2, and when it is mixed with its own vol. of chlorine and exposed to sunshine, it forms $COCl_2$, phosgene, chlorocarbonic acid gas, or oxychloride of carbon. When heated for a long time in contact with moist caustic potash, it is absorbed by that body with formation of potassic formiate,

$$CO + KHO = CHKO_2.$$

394. Carbon is only known to form one compound with sulphur, namely, carbonic disulphide, or sulpho-carbonic acid, CS_2. It is formed like the analogous oxygen compound, CO_2, by the direct union of its elements.

A tube of porcelain full of charcoal is run through a small furnace in a slanting direction, its lower end connected with a good condensing arrangement (it requires a much better one than shown in fig. 71), and its upper one fitted with a cork. The tube is heated to redness, the cork in the end removed, and a piece of sulphur dropped in, and the cork replaced. The sulphur melts, volatilises, and combines with the carbon, and the vapours produced pass on and condense in the cool part

of the apparatus. As one portion of sulphur is consumed another is added.

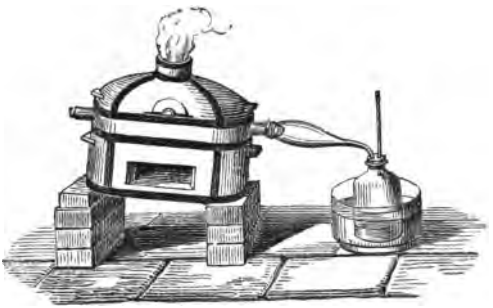


Fig. 71.

The product so obtained requires to be re-distilled to remove sulphur which it holds in solution. It is a very mobile liquid, with a most disgusting odour, and a remarkable power of refracting and dispersing light, which causes it to have a very brilliant appearance. It boils at 46° C., giving off a vapour which ignites at a temperature far below redness. This makes the preparation and use of carbonic disulphide very dangerous, since the easily formed and easily ignited vapour gives a very explosive mixture when mingled with air. Moreover, the vapour, when much inhaled, produces serious injury to the whole nervous system. It is possessed of remarkable solvent powers, and is used in the preparation and purification of some fatty, waxy, and resinous bodies.

395. Since sulphur is analogous to oxygen, CS_2 ought to have properties analogous to those of CO_2, as H_2S has analogies with H_2O. CO_2 combines with highly basic oxides to form carbonates, and CS_2 combines with the corresponding sulphides to form *sulpho-carbonates:*

$$CO_2 + K_2O = K_2CO_3, \text{ potassic carbonate,}$$
$$CS_2 + K_2S = K_2CS_3, \text{ potassic sulpho-carbonate.}$$

When a carbonate is acted on by hydric chloride or sul-

phate, we *suppose* (from analogy), that the metal is replaced by hydrogen,

$$K_2CO_3 + H_2SO_4 = K_2SO_4 + H_2CO_3,$$

but hydric carbonate is so unstable, that it immediately breaks up into carbonic dioxide and water.

When a sulpho-carbonate is treated in the same way, we do actually obtain hydric sulpho-carbonate, H_2CS_3, as an acid, oily liquid,

$$K_2CS_3 + H_2SO_4 = K_2SO_4 + H_2CS_3,$$

which is another argument in favour of the view that a solution of CO_2 really contains H_2CO_3.

CYANOGEN, $(CN)_2 = 26. = 2$ vol.

396. Is the only compound of carbon and nitrogen. It cannot be formed by the direct union of its elements. When nitrogen is passed over an intensely heated mixture of carbon and potassic carbonate, a compound having the formula CNK is produced. If the nitrogen is in the form of ammonia, or organic matters, the yield is much larger and the temperature needed is not so high. The body CNK, if distilled with dilute hydric sulphate, yields CNH, which is a feebly acid body known as prussic or hydrocyanic acid. The reaction is

$$2CNK + H_2SO_4 = 2CNH + K_2SO_4.$$

Prussic acid, when treated with mercuric oxide, has its hydrogen replaced by the metal,

$$2CNH + HgO = (CN)_2Hg + H_2O.$$

If $(CN)_2Hg$ be heated to redness in a tube (like that used for the preparation of oxygen) it decomposes, yielding metallic mercury, a gas having the formula CN, and a brown substance, which remains in the tube, having a composition identical with that of the gas.

The gas is called cyanogen; it is colourless, somewhat soluble in water, has a strong smell, which resembles, though in a remote degree, bitter almond oil, burns with a beautiful peach-blossom coloured flame, pro-

ducing carbonic acid and nitrogen. The brown substance is called paracyanogen, and is probably a polymeric modification of cyanogen, *i. e.*, contains $(CN)_n$ in its molecule.

397. Cyanogen combines directly with potassium to form CNK, and this body, as before stated, can have its potassium replaced by hydrogen.

Potassic and hydric cyanides resemble the corresponding compounds of chlorine in many ways, whence we are led to conclude that they are analogous in constitution, in the same way that we are forced to consider ammonium as a metal analogous to potassium.

Potassic chloride being KCl, potassic cyanide should be written $(CN)'K$, where $(CN)'$ acts the part of a monovalent radicle. But as we consider chlorine in the free state to be (Cl_2), free cyanogen should be $(CN)_2$. The density of cyanogen, as found by experiment, is 1·8064 (compared with air); but if the molecule was CN, the density would be $\frac{12 + 14}{2}$ as compared with hydrogen, or $\frac{13}{14·4} = 0·9028$ as compared with air. This number is sensibly half the real density (0·9028 × 2 = 1·8056).

The molecule of cyanogen is therefore $(CN)_2$. The symbol Cy is generally substituted for CN in the formulæ of the cyanides.

Hydrocyanic acid, or hydric cyanide, has very weak acid properties, but is the most active and deadly of poisons. It is very volatile, and the inhaling of its vapour is as dangerous as swallowing its solution. It is not advisable for students to experiment on this body without having the assistance of a teacher.

The soluble cyanides give with silver nitrate a white clotty precipitate of AgCN (or AgCy), which is insoluble in cold dilute hydric nitrate, but soluble in ammonia. It (AgCy) is distinguished from AgCl by dissolving in hot hydric nitrate, and by being decomposed by heat: $2AgCy = Ag_2 + Cy_2$.

The alkaline cyanides unite very readily with those of many of the heavy metals to form very stable double salts; *e.g.* the ferrocyanide of potassium, K_4FeCy_6. The alkaline cyanides, when fused in contact with oxygen or sulphur, or of bodies capable of yielding oxygen or sulphur, take up an atom of one or other of these elements to form M′CNO or M′CNS, cyanates or sulphocyanates. For the properties, mode of preparation and composition of the cyanates, ferrocyanides, &c., including Prussian blue, larger works must be consulted.

QUESTIONS ON CHAPTER XVII.

1. Mention the principal varieties of carbon, and the uses to which each is put.—Distinguish between the natural and artificial forms, and state how each is obtained.

2. How could it be proved that diamond, blacklead, lampblack, charcoal, and coke all essentially consist of carbon?

3. Explain how it is that porous carbon acts as a disinfectant.

4. If lead oxide be heated with lampblack, what happens?—Give the equation of the reaction.

5. If I burnt 5 grammes of pure carbon *completely*, what weight of the product should I obtain?—*Ans.* 18·3 grammes.

6. How much carbon could be burnt to carbonic acid by a kilogramme of air?—*Ans.* 86·25 grammes.

7. What volume of air would be required to burn 1 kilogramme of pure carbon?

8. How is "marsh gas" prepared; what is its calculated specific gravity, and what would be the weight of 1 litre of it?

9. How is it proved that the molecule of marsh gas contains 4 atoms of hydrogen?

10. What volume of marsh gas could be *completely* burnt by 10 litres of air?

11. How is olefiant gas prepared; why is it so called, and what are its other names?

12. What proof is there that the body to which the formula C_4H_8 is assigned is not the same as olefiant gas, C_2H_4?

13. What weight and what volume of oxygen is required to burn 100 grammes of olefiant gas?—*Ans.* 342·7 grammes, which = 240 litres.

14. What volume of oxygen would be required to burn a gallon of olefiant gas?—What volume of air would be required for the same purpose?—What would be the volume of carbonic dioxide resulting from the combustion? *Ans.* 1°. 3 gallons; 2°. 15 gallons nearly; 3°. 2 gallons.

15. (*a*) How is carbonic acid gas made?—(*b*) Give the equation representing the reaction.—(*c*) Describe its properties.—(*d*) State its principal natural sources.—(*e*) How would you distinguish it from nitrogen?

16. What evidence have you for considering carbonic dioxide to be an acid body?

17. Describe fully what takes place when a stream of carbonic acid gas is passed into lime water to saturation; also what occurs when the liquid so produced is boiled.

18. How would you prove that carbonic acid really consists of carbon and oxygen in the proportions stated by its formula?

19. What weight of carbonic acid is obtainable from 30 grammes of marble? (Ca=40.)—*Ans.* 13·2.

20. Give an equation of the reaction of hydric nitrate on potassic carbonate, and name each body used or produced.

21. Give the formulæ of the carbonates of K′, Na′, $(NH_4)'$, Ca″, Z[illegible], and Ag′.

22. What weight of carbonic acid could be obtained from 1000 grains of sodic carbonate? (Na=23.)

23. How is the carbonic acid of the air affected by growing plants?

24. How can carbonic oxide be made?—What are its properties?—What weight of carbon is contained in 1000 grains of it?—*Ans.* 428·57 grains.

25. Under what conditions would carbonic oxide be found in a common fire-place?

26. What volume of carbonic oxide would be obtained by completely reducing 100 cubic centimètres of carbonic acid by red hot charcoal?—*Ans.* 200 cc.

27. What weight of oxygen would be needed for the combustion of 1 lb. of carbonic oxide?—*Ans.* 57 lbs.

28. Compare the properties and mode of formation of carbonic disulphide with those of the corresponding oxygen compound?

29. What is cyanogen?—How is it prepared?—What element is it analogous to, and what should it form when it burns?

30. What is the molecular weight of cyanogen, and why is that number accepted instead of its half?

31. How would you prepare hydric cyanide?—In what reaction does it resemble hydric chloride?

32. A salt yields on analysis numbers corresponding to 9·09 per cent. of nitrogen, 20·77 per cent. of oxygen; and 70·13 per cent. of silver. What is its simplest formula?

33. A salt has been found to contain 28·17 per cent. of potassium, 25·64 per cent. of chlorine, and 46·19 per cent. of oxygen. What is its formula and its name?

34. A cliff contains 1,000,000 tons of pure chalk ($CaCO_3$). How many tons of carbon are there in the cliff?—*Ans.* 120,000 tons.

35. On an average, 6 out of every 10,000 parts by weight of air consist of carbonic dioxide. How much carbon is there in the air resting on a square yard of the earth's surface, taking the weight of air resting on a sq. in. as 15 lbs.—*Ans.* 3·2 lbs. nearly.

is made by adding a solution of potassic nitrate to one of hydric silicofluoride when it precipitates as a nearly transparent precipitate, which can hardly be seen without filtering it off from the liquid,

$$H_2SiF_6 + 2KNO_3 = K_2SiF_6 + 2HNO_3.$$

425. SILICA, SILEX, SILICIC DIOXIDE, and SILICIC ACID are various names for the only known oxide of silicon, SiO_2. Rock crystal is perfectly pure silica. Silica is prepared artificially by acting on a silicate by a strongly acid hydrogen salt, such as hydric chloride, just as carbonic dioxide is prepared from a carbonate. But most natural silicates resist the action of hydric chloride, so that it is necessary to prepare a suitable one.

Make a mixture of one part of silver sand, two parts pearl ash, and one part dried washing soda; half fill an earthen crucible with it, and heat the whole in a furnace (raising the temperature gradually) till the contents are in a state of tranquil fusion. Allow the crucible to cool, break it, and chip out the glass-like mass within. Make a solution (it requires long boiling), and put some of it into two glasses. To one portion add "hydrochloric acid," little by little, till the liquid is distinctly acid; a gelatinous precipitate of hydrated silica (silica combined with water) will be formed, which will *not dissolve* on addition of excess of the acid salt (H Cl). Pour the other, little by little, into an excess of "hydrochloric acid," somewhat diluted; no precipitate will be formed. Put this solution in a beaker, and stand it in another larger beaker containing water kept boiling. In the course of an hour or so the whole liquid will have become converted into a kind of transparent jelly, owing to the silica in the solution passing by the action of heat from the soluble into an insoluble modification.

We learn from these experiments that silica exhibits two forms—one soluble in "acids," and the other not; that the soluble form passes into the insoluble one by the action of heat, and that when it once has the insoluble form, excess of "acid" does not affect it.

Dry the two portions of gelatinous silica together with the chlorides accompanying it, by heating in an evaporating basin on the water bath, moisten the dry residue with aqueous hydric chloride, add water, transfer to a filter and wash till clean; dry and ignite the residue, which is perfectly pure silica. Silica so prepared is a light, white, gritty, tasteless powder, quite insoluble in water, and in all acid hydrogen salts, except hydrofluoric, but soluble in hot solutions of potash or soda.

426. If the crucible had been watched carefully at the time the mass first fused, it would have been observed that there was much frothing. Now frothing must arise from escaping gas blowing the mass up into bubbles, and the only gas here possible is carbonic dioxide. The sand used was nearly pure silicic dioxide, and at the high temperature it was capable of displacing the carbon compound, which accordingly escaped in the gaseous condition. Not only can silicic dioxide displace carbonic dioxide, but even sulphuric trioxide $S O_3$ and similar bodies, if the temperature be so high that they can volatilise and become removed from the mass.

The liberation of carbonic dioxide from fused alkaline carbonates can be more easily observed by fusing some of the latter (a mixture of three parts potassic carbonate and two parts sodic carbonate is best, because most fusible) in a platinum capsule over a Bunsen gas flame and throwing in a little finely powdered sand.

427. Another form of silica which is soluble in water alone is also known. It is prepared thus: make a dilute solution of silica in "hydrochloric acid" as described above, and pour it, to the depth of half an inch, into a vessel made by straining a piece of bladder, or better, parchment paper, over a gutta-percha hoop by means of another slightly larger hoop pressed over it and the sheet of wet membrane. Float the little arrangement on the surface of distilled water. After the lapse of six or seven hours test the outer water for the presence of chlorides (§ 101), and evaporate some to dryness, when a residue of chloride of potassium or sodium will be left. Treat this residue with water; nothing will remain undissolved, showing that the silica has not come through the septum. At the end of twenty-four hours change the water in the outer vessel, and continue to do so at like intervals till silver nitrate gives no precipitate in a portion either of the liquid from within or without the drum. The liquid in the drum is an aqueous solution of silica, free from the salts with which it was at first mixed. If it does not contain above 4% of silica, it will remain fluid for some time in a closed bottle, but gelatinises in the end. It may be concentrated to 14% by boiling in a flask. It is very slightly acid in reaction, and quite tasteless; it is coagulated (passes into the insoluble form as white of egg does when heated) by the action of minute quantities of carbonic acid or of earthy carbonates; therefore the addition of "hard water" causes it to become a jelly in a few minutes.

428. The separation of the hydric and sodic chlorides from the silica by the diaphragm in this experiment is owing to the phenomenon of liquid "diffusion" which is analogous to that of gases. Those molecules which have the greatest simplicity of constitution diffuse most rapidly, and certain bodies which are very complex hardly diffuse at all. Those bodies which diffuse readily are, for the most part, capable of assuming the crystalline state, and are therefore called "crystalloids." Those which are least diffusive often resemble "glue," and are called "colloids." Colloids allow crystalloids to diffuse through them, and Professor Graham calls the process "dialysis." The parchment paper is a colloidal substance, and is therefore permeable by crystalloids, like hydric and sodic chlorides; but not by colloidal bodies, such as this soluble variety of silica, the corresponding compound of tin $(S_n O_2)_n$, $(H_2 O)_m$, albumen, gelatine, &c., &c.; accordingly, when a mixture of a crystalloid and a colloid is submitted to dialysis, the former alone passes into the water outside the "dialyser."

429. The silicates, including those of hydrogen, are of very complex and somewhat uncertain composition and constitution. The best defined ones are those with the general formula, $M_4 Si O_4$, or $2 M_2 O, Si O_2$, but they readily unite with more silica to form $2 M_2 O, 2 Si O_2$, or $2 M_2 O, 4 Si O_2$, and these salts unite among themselves to form others (or mixtures) of still greater complexity.

Those silicates of the alkalies which do not contain a very great excess of silicic dioxide are soluble in water; those of other metals are nearly insoluble. The silicates of the alkalies unite readily with those of the alkaline earths (lime, baryta, &c.), and the heavy metals (*e. g.*, lead) to form very insoluble compounds, which possess the invaluable property of assuming a viscous condition before fusion when strongly heated. Such mixtures of various silicates constitute glass, the utility of which depends on its softening by heat, so as to admit of moulding.

Crown glass, such as is used for windows, &c., consists of a mixture

of silicates of calcium, aluminium, and sodium, containing about 69% of silica.

Flint glass, used for mirrors, drinking vessels, &c. consists of silicates of potassium and lead; it contains about 43% silica.

Bottle glass, a mixture of silicates of soda (very little), lime, iron (to which is owing its colour), and alumina. Silica = about 60%.

430. The silicates of most of the heavy metals have an intense colour. Fuse a bit of "lead glass" tubing, the size of a No. 8 shot, on a loop of platinum wire, in the *outer* flame of the blowpipe. Moisten the perfectly transparent bead with the lips, and take up with it a *minute* portion of one of the following substances, and fuse the bead again (in the outer flame).

Cobaltic oxide,	the glass will become		deep blue.
Cupric oxide,	,,	,,	green.
Manganic oxide	,,	,,	violet.
Ferric oxide	,,	,,	brown red, or yellow.

431. Silicon sulphide. Silicon forms only one compound with sulphur $Si S_2$, silicic disulphide, corresponding to carbonic disulphide. It is made by passing the vapour of $C S_2$ over an ignited mixture of silica and lampblack in a porcelain tube,

$$Si O_2 + C + C S_2 = Si S_2 + 2 C O.$$

The silicic sulphide condenses in the cool part of the tube in the form of long white silky needles, which can be volatilised in a stream of hydrogen.

Silicon forms a compound with nitrogen, the composition of which is not known.

432. The rare elements, zirconium and titanium, appear to belong to the same family as silicon, and to form the intermediate steps between it and tin. Unfortunately they have not been very closely studied, and it is accordingly not easy to show the gradual passage from the truly non-metallic to the metallic characters in the members of this group.

QUESTIONS ON CHAPTER XIX.

1. In what forms does silicon occur?

2. How would you prepare 1° amorphous silicon, 2° graphoidal silicon, 3° crystalline silicon?

3. Show in what respects silicon is metallic.

4. What is the probable composition of silicic hydride?

5. How is silicic chloride prepared?

6. How is silicic chloride made to yield evidence of the true atomic weight of silicon?

7. How is fluoride of silicon prepared?—What is the action of water on it?

8. If sand or powdered quartz be fused with sodic carbonate, what occurs?

9. Describe what happens when a solution of sodic silicate is (1°) gradually acidulated, (2°) poured into an excess of aqueous hydric chloride, and (3°) when the product of the last is heated for some time.

10. How is "soluble silica" prepared?

11. Explain the terms, "colloid," "crystalloid," and "dialysis."

12. What is glass?—How could glass be stained blue?

CHAPTER XX.

Tin, Symbol Sn. Atomic weight 118.

433. Is not found native, but in the form of oxide or sulphide. Its most abundant ore is cassiterite, or tinstone, which is principally procured in Cornwall, Devonshire, and Malacca. The extraction of the metal is effected by 1st freeing the rough ore from most of the earthy bodies mixed with it, by mechanical means; 2nd, reducing the oxide of tin left by the first process by heating it with charcoal or coal,

$$Sn\,O_2 + C_2 = Sn + 2\,C\,O.$$

Make a mixture of commercial stannic oxide (putty powder) with a quarter of its weight of lampblack and a little carbonate of soda, and heat the mixture to redness for half an hour in a covered earthen crucible. Remove the crucible from the fire and pour out the reduced tin on to a slab of stone.

Only one form of tin is known; it has the colour and lustre so well known as belonging to the thin sheets of iron covered with it which are called tin plate.

434. It melts at about 230° C., and on cooling crystallises readily, as can be shown by repeating with it the experiment described with bismuth in § 342, or by washing a piece of tin plate with very dilute aqua regia, when fern-like forms will develop themselves on the surface of the metal. When a bar of tin is bent it gives forth a crackling sound, which is very characteristic. Its specific gravity is 7·29. It conducts heat and electricity, though (for a metal) badly. It is soft and

malleable, *i. e.*, it can be beaten or rolled out into thin sheets as in tinfoil.

It does not oxidise by exposure to moist air, as is seen by its remaining bright for great lengths of time. When it is heated to redness in contact with air, it is slowly converted into stannic oxide. Heat a strip of tin plate to redness in the flame of a Bunsen lamp for some time; the tin on the surface will be converted into an earthy-grey body, consisting of the oxide and particles of unaltered tin. It dissolves in boiling hydric chloride with evolution of hydrogen, and it combines with chlorine, iodine, sulphur, and phosphorus.

When fused with other metals it combines in many cases to form alloys, which are very hard and tenacious; *e. g.*, with copper to form bronze and gun-metal.

435. Tin is not known to form any compound with hydrogen.

436. Two chlorides of tin are known with certainty, $Sn Cl_2$ and $Sn Cl_4$, stann*ous* and stann*ic* chlorides.

Stannous chloride, $Sn Cl_2$, or more probably $Sn_2 Cl_4$, is formed when tin is dissolved in boiling hydric chloride,

$$Sn + 2 H Cl = Sn Cl_2 + H_2.$$

The solution when evaporated and cooled deposits crystals of $Sn Cl_2, 2 H_2O$, and these when heated cautiously, lose their water, and leave a mass which can be distilled from a coated glass retort at a red heat. The distillate in this operation solidifies into a waxy mass of $Sn Cl_2$.

Stannous chloride dissolves completely in a small quantity of water, but is decomposed by an excess,

$$Sn_2 Cl_4 + H_2 O = Sn_2 O Cl_2 + 2 H Cl.$$

It is, therefore, necessary to add hydric chloride to the water used in preparing a solution of this body as a reagent. It rapidly combines with chlorine to form the tetrachloride; indeed, it even takes chlorine from many elements, and thereby acts as a reducing agent.

Add an acid solution of it to a solution of mercuric chloride, $Hg Cl_2$; at first a white precipitate of mercurous chloride will be formed, which will

afterwards become reduced to metallic mercury (as a grey powder) if an excess of the tin-salt be added.

It is used under the name of tin-salt as a mordant in dyeing.

Fasten a nut-sized piece of zinc to the end of a copper wire and suspend it in a filtered solution of 1 oz. of stannous chloride in a pint of water. The tin will be deposited on the zinc as dependent fern-like crystals.

$$Sn\,Cl_2 + Zn = Zn\,Cl_2 + Sn.$$

437. Stannic chloride, $Sn\,Cl_4 = 2$ vol., is formed by the direct union of chlorine and tin, the former being in excess, or by the addition of chlorine to stannous chloride, or by distilling together a mixture of stannic sulphate and common salt (NaCl).

$$Sn\,2\,SO_4 + 4\,NaCl = Sn\,Cl_4 + 2\,Na_2SO_4.$$

The last reaction is analogous to that which occurs between hydric sulphate and sodium chloride,

$$H_4\,2\,SO_4 + 4\,NaCl = H_4Cl_4 + 2\,Na_2SO_4,$$

only in place of four atoms of monovalent hydrogen we have one of tetravalent tin.

Stannic chloride is a colourless liquid which fumes in the air, is possessed of very caustic properties, and dissolves in water without decomposition, *unless the quantity of that liquid be very great*, and even then the decomposition is slow and very incomplete. If the two bodies be heated together in a sealed tube, decomposition is complete,

$$Sn\,Cl_4 + 2\,H_2O = Sn\,O_2 + 4\,H\,Cl.$$

438. Tin forms two bromides analogous to the chlorides. The iodides of tin can be made by heating 1 part granulated tin with 2 parts iodine, when the two combine violently, forming a mixture of $Sn\,I_2$ and $Sn\,I_4$. The latter can be sublimed out of the mass as yellowish red octahedral crystals, leaving the stannous iodide as a red crystalline mass. Stannous iodide is not decomposed by water, but the stannic salt is completely resolved at the boiling temperature into stannic oxide and hydric iodide,

$$Sn\,I_4 + 2\,H_2O = Sn\,O_2 + 4\,H\,I.$$

439. Stannous fluoride, $Sn\,F_2$ or $Sn_2\,F_4$, is obtained in crystals by evaporating a solution of stannous hydrate in hydric fluoride.

Stannic fluoride has not been obtained in a pure state, but when hydric fluoride is added in excess to a solution of an alkaline stannate, salts having the composition $M_2\,Sn\,F_6$ are obtained, which are not only analogous in composition to the fluo-silicates, but are also isomorphous (having the same crystalline form).

440. The oxides of tin are two, SnO and SnO_2. SnO (or Sn_2O_2), stannous oxide is prepared by precipitating a solution of stannous chloride by a solution of sodic carbonate, whereby stannous hydrate is formed.

$$Sn_2Cl_2 + Na_2CO_3 + H_2O = Sn_2O_2,\ H_2O + 2\,NaCl + CO_2.$$

(The carbonic dioxide goes off because stannous oxide is too feebly basic to hold so feebly-acid a body.) This is washed and dried and heated in a tube kept filled with carbonic dioxide.

$$Sn_2O_2,\ H_2O = Sn_2O_3 + H_2O.$$

So prepared, stannous oxide is a brown powder, which is not altered by exposure to air, but which combines with oxygen so readily at high temperatures that it can be set fire to by a red-hot body; it then glows like tinder, and is converted into stannic oxide. It reacts with various hydric salts to form the corresponding stannous salts, *e. g.*,

$$Sn_2O_2 + 4\,HCl = Sn_2Cl_4 + 2\,H_2O.$$

When boiled with strong potash or soda, it is converted into a stannate of the alkali metal with *separation of metallic tin*,

$$Sn_2O_2 + 2\,KHO = K_2SnO_3 + Sn + H_2O.$$

Stannous hydrate prepared as above is a white precipitate, which dissolves both in hydric salts and in alkalies (fixed); it acts as a reducing agent, owing to its strong tendency to become stannic oxide.

441. Stannic oxide, $Sn\,O_2$, is readily prepared either by fusing tin at a high temperature in contact with air, or by

oxidising the metal by hydric nitrate and igniting the white powder so produced.

It is a yellowish powder, the grains of which are so hard that it is used as a polishing powder (putty powder). When heated it becomes dark yellow, but recovers its usual colour on cooling. It is not dissolved by acid hydrogen salts, but when heated in a tube and submitted to the action of chlorine gas, it yields stannic chloride, $Sn\ Cl_4$, without the assistance of the simultaneous action of carbon.

$$Sn\ O_2 + Cl_4 = Sn\ Cl_4 + O_2.$$

This, with its easy reduction by carbon (and hydrogen), shows that tin does not hold oxygen so forcibly as silicon does. Stannic oxide forms two hydrates possessed of acid properties, the one, $H_2\ Sn\ O_3$, called stannic acid or hydric stannate, corresponding to the hypothetical $H_2\ C\ O_3$, and the other, $H_{10}\ Sn_5\ O_{15}$, metastannic acid, or hydric metastannate.

The first is precipitated in a gelatinous form by the addition of hydric chloride, not in excess, to an alkaline stannate,

$$K_2\ Sn\ O_3 + 2\ H\ Cl = 2\ Na\ Cl + H_2\ Sn\ O_3.$$

When recently precipitated, it is soluble in excess of cold hydric nitrate or hydric chloride, forming a stannic salt, *e. g.*,

$$H_2\ Sn\ O_3 + 4\ H\ N\ O_3 = 3\ H_2\ O + Sn\ (N\ O_3)_4, \text{ stannic nitrate,}$$

which is, however, very unstable, as the basic properties of stannic hydrate are feeble.

If it is dried and pretty strongly heated, it becomes stannic oxide, which is insoluble in acid liquids. Compare with silicic hydrate (§ 425). Its acid properties are much more strongly marked than its basic ones. It is acid to litmus paper, it dissolves easily in alkalies, forming salts, which can be crystallised, *e. g.*,

$$2\ K\ H\ O\ +\ H_2\ Sn\ O_3\ =\ K_2\ Sn\ O_3\ +\ 2\ H_2O.$$

These same stannates can also be prepared by fusing stannic

oxide with the caustic alkalies. They are used in calico printing as mordants.

442**. Metastannic hydrate, $Sn_5 H_{10} O_{15}$, or $(Sn H_2 O_3)_5$ is formed as a yellowish-white powder when tin is acted on by slightly diluted hydric nitrate. It is insoluble in concentrated acid hydrogen salts, but dissolves in solutions of potash or soda to form the metastannates, $Sn_5 K_2 H_8 O_{15}$, or $Sn_5 Na_2 H_8 O_{15}$, which are gummy and uncrystallisable.

443. Sulphur forms two well defined compounds with tin, corresponding to stannous and stannic oxides.

Stannous sulphide is made by the direct union of sulphur and tin.

By heating sulphur and tinfoil together in a test tube, Sn S will be formed as a leaden grey mass; or, by precipitating a solution of stannous chloride with hydric-sulphide, as a brown powder,

$$Sn_2 Cl_4 + 2 H_2 S = 2 Sn S + 4 H Cl.$$

It does not dissolve in solutions of pure alkaline sulphides; it is therefore not a sulphur acid. It dissolves however in alkaline sulphides containing an excess of dissolved sulphur, to form sulpho-stannates; from which strongly acid hydric salts throw down a yellow precipitate of hydric sulpho-stannate, $H_2 Sn S_3$, corresponding to $H_2 C S_3$ (§ 395).

444. Stannic sulphide, $Sn S_2$, is made by precipitating an acid solution of stannic chloride by hydric sulphide,

$$Sn Cl_4 + 2 H_2 S = Sn S_2 + 4 H Cl,$$

as a yellow amorphous powder, easily soluble in alkaline sulphides to form sulpho-stannates. It is obtained in a crystalline form by heating a mixture of equal parts of tin-filings, sulphur, and sal ammoniac nearly to redness in a flask half buried in a sand bath. Ammonic chloride and excess of sulphur then volatilise, and stannic sulphide remains as a glittering yellow body, known as "aurum musivum," or mosaic gold.

445. Tin is not known to form any compound with nitrogen, but combines with phosphorus, arsenic, and antimony to form

alloys. The compound of nine parts tin and one part antimony constitutes Britannia metal.

Tin does not unite with carbon or silicon.

The tests for the presence of tin in acid solutions are—

1°. Sulphuretted hydrogen produces a brown (in stannous) or yellow (in stannic) precipitate soluble in alkaline sulphides, containing dissolved sulphur, but not in ammonic carbonate.

2°. Potash or soda gives white precipitates of stannous or stannic hydrate.

3°. Iron foil or wire in presence of excess of hydric chloride completely reduces any stannic salt to a stannous one, and the reduced solution gives a white or grey precipitate with solution of mercuric chloride (see § 436).

4°. When the solution is evaporated, mixed with carbonate of soda, and the mass ignited on charcoal in the inner flame of the blowpipe, a malleable bead of metal is formed, which bead will dissolve in hydric chloride, and give all the reactions of stannous compounds.

QUESTIONS ON CHAPTER XX.

1. What is the most important ore of tin, and how is the metal extracted therefrom?

2. What are the physical and chemical properties of tin?

3. How are the two chlorides of tin prepared?

4. What reaction takes place when stannic sulphate is heated with sodic chloride?

5. What would the formula of potassic and baric fluo-stannates be?

6. How is stannous hydrate prepared, and what change does it undergo when boiled with excess of potassic hydrate?

7. What is formed when tin is acted on by excess of hydric nitrate?—What is formed when it is ignited?

8. Is stannic hydrate acid or basic?

9. What salts are the stannates most analogous to?

10. Describe the mode of preparation and the properties of the sulphides of tin.

11. How is the presence of tin in a solution detected?

CHAPTER XXI.

Boron, Symb. B. Atomic weight 11.

446. This element, which constitutes a family by itself, is never found free, but always in combination. The borates of hydrogen, sodium, and calcium, constitute the most abundant source of the element. Hydric borate is found in the steam which issues from clefts in the rocks of many volcanic districts. It is obtained by condensing the vapour in pools of water formed over the openings of the clefts, and after addition of soda evaporating the solution so obtained by the heat of a jet of steam from another hole.

447. The only known oxide of boron, B_2O_3, when fused with potassium or sodium, yields amorphous boron, which closely resembles amorphous silicon. It burns readily in air or oxygen, forming B_2O_3. When fused with alkaline carbonates it liberates carbon.

Graphitoïdal boron is made by fusing aluminium and boric oxide together, with fluor spar as a flux, when one portion of the aluminium reduces the boron which dissolves in the remaining metal, and separates therefrom on cooling in copper-coloured hexagonal scales which refuse to burn in the air. They are separated from the excess of aluminium by dissolving the latter in a dilute hydric chloride. Crystalline boron is made by the same process as the last (suppressing the fluor spar), only the heat employed is much more intense and prolonged. Well defined crystals are left, when the metal is dissolved away, which are sometimes transparent. They are nearly as hard, and have almost as great refractive and dispersive power, as diamonds. They have never been obtained free from carbon and aluminium, so that it is possible that true crystalline boron has quite other properties.

Boron forms no hydride.

448. Boric chloride $BCl_3 = 2$ vol. Is prepared like silicic chloride, substituting B_2O_3 for SiO_2, or by the direct action of chlorine on dry amor-

phous boron. It is a colourless fuming mobile liquid, which boils at 170° C. Its vapour density is 4·06 times as great as air at the same temperature. It is decomposed completely by water.

$$BCl_3 + 3H_2O = H_3BO_3 + 3HCl.$$

449. Boric fluoride, $BF_3 = 2$ vol. Prepared by action of hydric fluoride on boric oxide. A mixture of boric oxide, fluor spar (CaF_2), and hydric sulphate is distilled together, when boric fluoride escapes as a gas.

$$3CaF_2 + B_2O_3 + 3H_2SO_4 = 3CaSO_4 + 3H_2O + 2BF_3,$$

which can be collected over mercury. It is dissolved by $\frac{1}{700}$ of its vol. of water. A comparatively weak solution of the gas when cooled deposits hydric borate, and hydrofluoboric acid remains in solution.

$$4BF_3 + 3H_2O = 3BHF_4 + H_3BO_3.$$

If the student attempts to prepare the solution of boric fluoride, he should be careful to lead the gas below the surface of mercury at the bottom of the water, or the solution of the gas will take place so rapidly that the water will rush up the delivery tube into the generating flask.

450. The only known oxide of boron is B_2O_3 boric trioxide, or boracic acid, which is obtained by igniting hydric borate, H_3BO_3,

$$2H_3BO_3 = B_2O_3 + 3H_2O,$$

as a glassy mass, which at a red heat is capable of expelling nearly all other acid oxides from their compounds with basic oxides. When thrown into water it again unites with it to form hydric borate.

Hydric borate is made by adding hydric sulphate to a concentrated hot solution of borax (sodic biborate) till the solution is strongly acid to litmus paper, and then allowing the whole to cool. Hydric borate then crystallises out, and can be partially purified by draining well on a porous tile and recrystallising.

It forms pearly, greasy feeling, indistinct crystals, which dissolve in water and alcohol, and communicate a bright green tint to the flame of the latter when it is burnt. Its solution turns blue litmus paper the same colour that carbonic acid does, *i.e.*, a wine-red colour; but it acts in a special and characteristic way on turmeric paper, which it turns from yellow to reddish-

brown, even in presence of free hydric chloride.* The brownish colour is turned black by sodic carbonate solution.

Hydric borate evaporates pretty readily in vapour of water; it is, therefore, impossible to evaporate a solution of it without great loss.

451. The borates are almost more complex, and are certainly less interesting, than the silicates; the most important is borax, which is largely used as a flux in soldering certain metals, and as a constituent of certain enamels and glazes; its composition is represented by Na_2O, B_2O_3 + Aq. All borates are somewhat soluble in water, therefore it is impossible to precipitate the whole of a given quantity of boracic acid from solution.

452. Boron when heated in vapour of sulphur forms boric sulphide, B_2S_3, which is a white solid body, not volatile by itself, but capable of evaporating in a current of hydric sulphide. It is rapidly decomposed by water.

$$B_2S_3 + 3H_2O = B_2O_3 + 3H_2S.$$

453. Boron forms a compound with nitrogen with great facility. The two elements unite when nitrogen is passed over strongly ignited amorphous boron, the action constituting one of the very few instances of the direct union of nitrogen with another element. A simple way of preparing this body is to heat to redness a mixture of two parts sal ammoniac and one part dry borax in a covered porcelain crucible, and then to dissolve out the sodic chloride formed by boiling water. Nitride of boron, $B''N'''$, is a white amorphous powder, without taste or smell, without action on acids or alkalies, infusible and non volatile. If ignited in the oxyhydrogen blow-pipe flame, it burns with a greenish flame.

Other compounds of boron are unimportant.

The presence of a borate is detected by,

1°. Mixing the suspected body with alcohol, adding an excess of strong oil of vitriol, warming, setting fire to the vapour, and stirring. A green-edged flame gives the required indication. Copper, which behaves in a like manner, must be absent.

2°. Acidulating the solution with hydric chloride, moistening

* The reaction is best shown by drying gently a slip of turmeric paper, one half of which has been dipped in an acidified solution of borax.

a slip of turmeric paper therewith and drying the slip, when it becomes of a peculiar brown colour if a borate be present.

3°. Mixing the suspected body with three times its weight (about) of a mixture of fluor spar and hydropotassic sulphate, and igniting a portion of the mixture on platinum wire in the blow-pipe flame, a green flame, due to boric fluoride, will be produced.

453*a*. OZONE.—When treating of oxygen, it would have been proper to have mentioned the existence of an allotropic form of it, which is known under the above name. When a series of electric sparks, or, better, the continuous silent "brush discharge," is passed through perfectly pure dry oxygen, the gas undergoes a diminution of volume which in no case amounts to more than one-twelfth of the total volume. At the same time it acquires new properties; it becomes much more energetic, it converts silver into its oxide at ordinary temperatures, bleaches indigo, and causes the oxidation of most bodies which are capable of oxidation; it has a peculiar and characteristic smell, and liberates iodine from the iodides.

It appears, on evidence which cannot here be given, that the molecule of ozone probably contains three atoms of oxygen, if that of ordinary free oxygen contains two.

The oxygen liberated from water by the electric current; and air, which has been exposed for some time to moist phosphorus; exhibit most, if not all, the properties which really ozonised oxygen exhibits, and therefore probably contain ozone.

QUESTIONS ON CHAPTER XXI.

1. What are the forms in which boron is mostly found?
2. What forms is boron known to assume, and how is each prepared?
3. How would you prepare boric fluoride? what should be the weight of 1 litre of its vapour, if it were possible to determine it, at 0° C., and ·760 metres bar. press.?
4. How is boric trioxide prepared?
5. What is there peculiar about the action of a solution of "boracic acid" on vegetable colours?
6. What is borax?
7. What is remarkable about the behaviour of boron to nitrogen?
8. By what reaction is the presence of a borate detected?

CHAPTER XXII.

454. THE atomic theory, or, more properly, the theory resting on the atomic hypothesis, as devised by Dalton, has undergone several modifications, in the nature of extensions and developments. Thus, speaking generally, Dalton, or his immediate successors, found that hydrogen combined in the smallest proportions with other elements, and therefore supposed it to have the lightest atoms, and accordingly adopted it as the unit or standard of atomic weight. One part by weight of hydrogen united with eight of oxygen, or with thirty-five and a half parts of chlorine, and these weights of oxygen and chlorine respectively united with the same quantity (108 parts) of silver, which quantity was thus found to be equivalent in combining power to one part of hydrogen; and, equivalent weights being supposed to be the same as atomic weights, silver was taken to have an atomic weight of 108.

The terms atomic weight and equivalent weight were used almost indiscriminately.

455. Then other facts rose into notice; *e.g.*, that while the hydrogen in hydric chloride could not be divided, that in water was divisible by two (§ 56), that in ammonia by three (§ 213), and that in marsh gas by four (§ 369), whence it was obvious that these bodies contained respectively at least one, two, three, and four atoms of hydrogen in the smallest portion of them which could exist, whereas the other elements united to these quantities of hydrogen could not be divided, and were therefore presumably single atoms. Further, the quantities

of the above typical compounds which contained one, two, three, and four atoms of hydrogen, all occupied the same space, and were therefore comparable quantities, and these equal volumes contained weights of chlorine, oxygen, nitrogen, and carbon, which were to one another as 35·5, 16, 14, and 12, which represented therefore the atomic weights of Cl, O, N, and C.

456. But these atomic weights are no longer equal to the equivalent weights in all cases; thus, 16 parts of oxygen unite with twice 108 parts of silver, or twice 1 part of hydrogen, and therefore its atom is equivalent in combining power to two atoms of chlorine, which, as before shown, is equal, atom for atom, (in combining power) to hydrogen, and the atom of oxygen is therefore called divalent.

By reasonings of a parallel nature, nitrogen is shown to be trivalent, and carbon tetravalent, and other elements are shown to belong to one or other of the four classes represented by these typical ones, from their analogies to them :—

Monovalent elements.	Divalent elements.	Trivalent elements.	Tetravalent elements.
H'	O''	N'''	C^{iv}
F'	S''	P'''	Si^{iv}
Cl'	Se''	As'''	Sn^{iv}
Br'	Te''	Sb'''	Ti^{iv}
I'	—	Bi'''	Pt^{iv}
—	Ca''	—	
K'	Ba''	B'''	
Na'	Mg''	Au''	
Ag'	Fe'' (?)		
—	Mn''		
	Zn''		
	Cu''		
	Hg''		

457. It is to be remarked, however, that the considerations which determine the valency of an element are of such a nature, that different combining values can be assigned to one and the

same element. Thus in the cases of nitrogen and its group of elements: though in the molecule of ammonia there are three atoms of the monovalent hydrogen, yet in ammonic chloride, $N H_4 Cl$, nitrogen is in union with *five* monovalent atoms, and may, therefore, be said to be pentavalent. Phosphorus and antimony form pentachlorides, as well as trichlorides, and are so far pentavalent. It is worthy of observation, however, that none of the compounds, in which these elements appear to be pentavalent, occupy the normal two volumes in the state of vapour, but always four volumes, as if they consisted of loosely attached molecules of $N H_3$, and $H Cl$; $P Cl_3$, and Cl_2; and $Sb Cl_3$, and Cl_2, respectively.

458. If an element having the power to combine with, say four atoms of a monovalent element, unites with only three such atoms, then it is evident that in the compound so formed there is, so to speak, one unsatisfied power of combination, or if it unites with one atom of a trivalent element, still its combining power remains unsatisfied to the extent of one unit. Take the case of carbon and nitrogen in the compound $C^{iv} N'''$, cyanogen, which acts in so many ways like monovalent chlorine. It not only combines directly with potassium, as chlorine does, but it also forms a hydrogen salt, $H' (C^{iv} N''')'$; and, moreover, does not exist in a free state, without having its odd combining capacity satisfied by another equal quantity of itself; $(C^{iv} N''')'$ being monovalent, combines with another $(C^{iv} N''')'$ to form $(C^{iv} N''')_2$, as Cl' combines with Cl' to form Cl_2. Hydrogen and oxygen form peroxide of hydrogen by the union of two hydroxyls $(H' O'')' + (H' O'')' = (H' O'')_2$; this hydroxyl being monovalent plays the part of a monovalent element, just as cyanogen does. Again, carbon and oxygen unite to form carbonic oxide, $C^{iv} O''$, in which carbon has two of its combining powers unsatisfied, and which accordingly acts as a divalent element $(C^{iv} O'')''$ in uniting directly with O'' to form $C^{iv} O''_2$, and with Cl'_2 to form $C^{iv} O'' Cl'_2$, which are *complete* molecules.

459. In the cases where two elements unite in more complex proportions, *e. g.*, in ethylene, $C_2 H_4$, and its homologues, it is

shown by experiments which belong to the domain of organic chemistry, that elements of like kind unite and partially satisfy one another's combining powers, thus, C_2H_4 is shown to be built up in a manner that can be represented by $\begin{matrix} H-C-H \\ H-C-H' \end{matrix}$ that is, two of the four combining powers of each carbon are satisfied by combination with the other carbon, while the remaining two powers of each atom are satisfied by the hydrogen.

460. When hydric sulphate (H_2SO_4) is submitted to the action of phosphoric pentoxide, it loses the elements of water, and yields sulphuric trioxide, SO_3, which, if again brought into contact with water, regenerates hydric sulphate. These reactions give us reason to believe that hydric sulphate contains a molecule of SO_3 united with one of H_2O, and if we write its formula in such a way as to give expression to that belief, thus, SO_3, H_2O, we obtain a formula which assigns a reason for the actions above mentioned, and call that formula (though not very aptly), a Rational formula; whereas, when all the like elements were written together, we had an Empirical formula.

461. As a rational formula is one which assigns a reason for some one or more reactions of the body represented, there may obviously be a great number of rational formulæ for the same body, if it exhibits a great number of reactions and decompositions.

If hydric sulphate be submitted to the action of phosphoric oxichloride (§ 286), the remaining liquid when distilled yields a chlorohydrated sulphuric acid, having the composition, HSO_3Cl. The reaction which occurs is

$$3H_2SO_4 + POCl_3 = PO_4H_3 + 3HSO_3Cl.$$

When this body in its turn is submitted to the further action of the oxichloride, it again reacts,

$$3HSO_3Cl + POCl_3 = PO_4H_3 + 3SO_2Cl_2.$$

In the first reaction, each molecule H_2SO_4 lost the elements of

hydroxyl, and got an atom of chlorine in exchange, and in the second reaction, this substitution of chlorine for hydroxyl was repeated. If now we write the formula of hydric sulphate in such a way as to show that there are two hydroxyls in it, thus, $S O_2 H O HO$, we obtain for it a second rational formula, which enables us to show with great clearness the nature of the changes which it underwent by the action of the phosphoric oxichloride,

1st. $(S O_2)'' H O, HO$, lost H O, and acquired Cl forming $(S O_2)'' H O, Cl$.
2nd. $(S O_2)'' H O, Cl$ lost H O, and acquired Cl forming $(S O_2)'' Cl Cl$.

$S O_2 Cl_2$, when acted on by water, regenerates successively $S O_2, HO Cl$, and $S O_2, H O, H O$. By similar experiments, or by analogy, we are led to adopt rational formulæ similar to that of hydric sulphate for other hydric salts, thus,

$H N O_3 = (N O_2)' H O$:—$H Cl O = (Cl)' H O$.
$H_2 C O_3 = (C O)'' H O, H O$:—$H_3 P O_4 = (P O)''' H O, HO, H O$.

And as metallic salts are the result of substituting a metal for hydrogen in hydric salts, we obtain rational formulæ for them by writing the symbol of the given metal in place of an equivalent quantity of hydrogen in these formulæ, or their multiples, *e.g.*,

$Na_2 S O_4 = (S O_2) Na O, Na O$, and $Ca S O_4 = (S O_2) O Ca'' O$.

The further development of the ideas concerning the constitution of compounds cannot be well attempted without drawing for instances upon organic chemistry.

462. It has been shown that many elements exist in more than one form, *e. g.*, oxygen in the ordinary form, and as ozone; (p. 273), sulphur, phosphorus, and carbon in many forms; and that these modifications of one and the same element are so

different that they might be mistaken for totally distinct bodies, did they not yield equal quantities of the same product of combustion, *e. g.*, 1 gramme of clear or of red phosphorus when burnt will yield the same weight of phosphoric pentoxide. If we seek an explanation of this most curious fact of allotropy, we can only find it by assuming the truth of the atomic hypothesis, and supposing that the various forms of a free element consist of molecules containing a different number of atoms.

That the same element can have different molecular weights, and must consequently be capable of forming self compounds containing a varying number of *parts*, is a strong argument in favour of the atomic constitution of matter.

463. Again, the fact that elements which are just leaving the state of combination are possessed of more energetic combining powers than when free,—that nascent oxygen is possessed of the power of *reducing* some oxidised bodies,—and that heat is evolved on the sudden decomposition into their elements of bodies like the chloride and iodide of nitrogen,—all point to the fact that free elements consist of something different from the same element in combination; and that this difference is due to one part of the given element uniting with another part, a thing which receives no explanation on any other hypothesis than that of the existence of atoms.

The reducing power of nascent oxygen is illustrated by the action of hydric dioxide on silver oxide,

$$Ag_2O + H_2O_2 = H_2O + Ag_2 + O_2.$$

One atom of oxygen from H_2O_2 *unites* with that of the unstable silver oxide to form a molecule of free oxygen. The decomposition of chloride of nitrogen consists in the liberation of its elements, NCl_3 becoming free nitrogen and chlorine. If it were a case of simple un-combining, heat would be *absorbed;* but as heat is evolved, there is evidence that the atoms of nitrogen and chlorine unite among themselves to form molecules,

$$\left.\begin{matrix} NCl_3 \\ NCl_3 \end{matrix}\right. = \left.\begin{matrix} N \\ N \end{matrix}\right\} + 3\left\{\begin{matrix} Cl \\ Cl \end{matrix}\right\},$$

and that the energy of combination of nitrogen with nitrogen and of chlorine with chlorine is greater than that of chlorine with nitrogen.

464. Those quantities of the elementary bodies (with one or two apparent exceptions), which on chemical evidence appear to be atomic weights, are found also to act as comparable quantities in their relations to heat. Thus it takes sensibly as much heat to raise 23 grammes, ounces, &c., of sodium 1° C. as to heat 39 parts of potassium, 108 of silver, or 210 of bismuth, through the same range of temperature.*

465. Now what we have learnt of the composition and properties of those few forms of matter which are treated of in this work, has led us to form an idea that matter, as we know it, consists of parts which act as they would act if indivisible: which parts are alike in the same kind of matter, but are unlike in different kinds. Of the absolute size or weight of these parts, which we call atoms, we know nothing, but we have abundant evidence of their *relative* weights.

As none of the chemical facts with which we are acquainted have been explained on any other assumption than that of the atomic constitution of matter, we have the same kind of evidence of the existence of atoms as we have of the existence of any of the grosser forms to which aggregation of those atoms gives rise.

We have and can have no knowledge of matter, except that derived from the way in which it directly or indirectly affects our senses. We do not doubt of the existence of hydrogen, because we cannot see, smell, touch, or taste it; for we can prove that it occupies space, has weight, burns, reduces oxides, &c., &c., which facts are consistent only with the existence of some form of matter different from all other matter. How, then, is it possible to deny the existence of atoms, simply because they cannot be isolated, and exhibited to view, when all the facts known to us are consistent with their existence, and when most can only be explained on the assumption of their actual being?

* Some of these arguments are borrowed from a recent paper of Professor Williamson's on the "Atomic Theory," in the Journal of the Chemical Society.

GENERAL QUESTIONS.

1. A body yields, by analysis, 43·75 per cent. of nitrogen, 6·25 per cent. of hydrogen, and 50·0 per cent. of oxygen. What is its formula and its name? — *Ans.* Simplest formula from analysis = NH_2O; no such body is known; so double this = $N_2H_4O_2 = NH_4NO_2$ = ammonic nitrite.

2. A solution of potassic chlorate was reduced to chloride, and then precipitated by an excess of argentic nitrate. 7·275 grammes of argentic chloride were obtained. What was the weight of the chlorate in the solution?—*Ans.* 6·21 grammes.

3. Give equations representing the most useful method of preparing each of the following bodies:—Oxygen, hydrogen, nitrogen, hydric nitrate, nitric oxide, nitrous oxide, ammonia, carbonic acid, marsh gas, olefiant gas, sulphurous acid gas, sulphuretted hydrogen, chlorine, hydric chloride, hydric iodide, potassic chlorate, trihydric phosphate, phosphuretted hydrogen.

4. Give the formulæ and systematic names of "salt," "Epsom salts," "spirits of salt," and "blue vitriol."

5. Classify the common metals according to their equivalency. Give the formula of the characteristic oxide, chloride, and hydrate of each.

6. How much heavier or lighter than air are the following gases and vapours:—Hydrogen, nitrogen, water, ammonia, nitric tetroxide, nitrous oxide, carbonic dioxide, and nitric oxide.

7. Explain what is meant by the terms monobasic, dibasic, and tribasic acids, and give instances of each class.

8. How much heavier than hydrogen are the following gases and vapours:—Hydric chloride, hydric iodide, iodine, hydric sulphide, hydric sulphate (4 vol.), sulphurous acid gas, sulphur.

9. When sulphide of iron is dissolved in dilute hydric sulphate, what gas is given off, what properties has that gas, and what does it form when it burns?

10. Give the formulæ of:—(*a*) Potassic hydrate; (*b*) potassic oxide; (*c*) potassic nitrate; (*d*) cupric oxide; (*e*) cupric nitrate; (*f*) nitrous oxide; (*g*) hydric sulphate; (*h*) black oxide of manganese; (*i*) zinc sulphate; (*k*) zinc chloride.

11. How would you determine, by *experiment*, the proportion of nitrogen in an organic body?

12. Give an outline of the atomic theory.

13. (*a*) What gas most resembles oxygen? (*b*) How is it prepared? (*c*) How can it be distinguished from oxygen?

14. Explain the meaning of the following equations; name each body:—

(*a*) $CaO + 2NH_4Cl = 2NH_3 + CaCl_2 + H_2O$.
(*b*) $C_2H_4 + O_6 = 2CO_2 + 2H_2O$.
(*c*) $NH_4NO_3 + KHO = KNO_3 + NH_3 + H_2O$.
(*d*) $2NH_3 + H_2SO_4 = (NH_4)_2SO_4$.
(*e*) $NH_4NO_3 = N_2O + 2H_2O$.
(*f*) $NaNO_3 + H_2SO_4 = HNO_3 + NaHSO_4$.
(*g*) $NH_4Cl + AgNO_3 = NH_4NO_3 + AgCl$.

15. Name each body used or produced in the reactions represented by—

(*a*) $H_2O + Na = H + HNaO$.
(*b*) $4H_2O + 3Fe = H_8 + Fe_3O_4$.
(*c*) $KNO_3 + H_2SO_4 = HNO_3 + HKSO_4$.
(*d*) $2HCl + Fe = H_2 + FeCl_2$.
(*e*) $KHO + HNO_3 = KNO_3 + H_2O$.

N.B.—Write down the equations before naming the bodies.

16. Give equations representing the formation of the following bodies:—(*a*) Marsh gas; (*b*) olefiant gas; (*c*) hydric chloride; (*d*) hydric iodide; (*e*) sulphuric dioxide; (*f*) potassic chlorate; (*g*) hydric fluoride; (*h*) silver chloride.

17. Give equations representing the reaction of—(*a*) Sodium and water; (*b*) iron and water (at a red heat); (*c*) copper and hydric nitrate; (*d*) copper and hot strong hydric sulphate; (*e*) charcoal and hot strong hydric sulphate; (*f*) potassic nitrate and hydric sulphate; (*g*) sodic chloride and hydric sulphate; (*h*) chlorine and sulphuretted hydrogen.

18. What is the distinction between an acid and an alkali? What is meant by the term "Salt"?

19. What weights of oxygen, chlorine, and bromine are chemically *equivalent* to 12 parts by weight of sulphur?

20. Write out a table of the oxygen compounds of the nitrogen family of elements.

21. Also write out a table of the compounds of the nitrogen family containing oxygen and hydrogen.

22. A mixture of oxygen and nitrogen measures 35 cubic centimetres at the normal temperature and pressure; 35 c. c. of hydrogen (at same temp. &c.) are added, and the mixture exploded, 25 c. c. of gas remain. What was the composition of the original gas?—*Ans.* 4 vol. N, 3 vol. O.

23. 40 c. c. (at 0° C., &c.) of a gas containing oxygen and nitrogen were mixed with 37 c. c. of hydrogen and exploded; 32 c. c. of gas remained. What was the composition of the original gas?—*Ans.* $\frac{O = 15}{N = 25}$ cubic cent.

CRYSTALLINE SYSTEMS.*

WITH some rare exceptions, all bodies, whether simple or compound, in passing from the fluid to the solid state, manifest the peculiarity of structure which is expressed by the term *crystalline;* and vast numbers are found, especially in the mineral kingdom, naturally in this condition. When a body in this state is broken, its surface of fracture will present the appearance of a multitude of pointed asperities, which will at first seem to be irregular, but, when submitted to the microscope, will be found to have a certain uniform geometrical structure.

From this and other observations it has been inferred, that crystallised bodies consist of aggregations of solid particles of regular geometrical figures, all the particles or molecules of the same mass having the same form.

When a crystallised body is split, it is found that its division is much more easily effected in some directions than in others. Such directions are called *planes of cleavage*, and are, in fact, parallel to the faces of the component crystals.

The relative directions of the planes of cleavage supply one of the means of determining the forms of the crystals.

The exposition of the properties of crystals forms the part of physical science called *crystallography.*

CRYSTALLINE SYSTEMS.—Although they are infinitely various, crystalline forms have been reduced to a very limited number of classes. Some forms

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* Taken from "Lardner's Chemistry."

are mere modifications of others of a more simple nature. Others are produced by the combination of the more simple forms.

CENTRE.—Within every crystal there is a certain point which divides into equal parts every line passing through it and terminated in the faces or edges of the crystal. This point is called the *centre* of the crystal, from its analogy to the centre of a circle, which divides the diameters into equal parts.

DIAMETERS.—Lines passing through the centre and terminated in the crystal are called *diameters.*

AXES.—Diameters so placed that a plane passing through them will divide the crystal into equal and similar solids, are called *axes.* The crystal is therefore disposed symmetrically around each of its axes.

These axes are distinguished by very important optical properties, which often serve as a convenient method of determining their direction.

All the varieties of crystalline forms have been reduced to six classes, called *crystalline systems,* which are severally characterised by the number, relative position, and relative length of the axes.

1°. THE REGULAR SYSTEM has three equal axes, each of which is at right angles to the plane of the other two.

This system includes the *cube* or *regular hexahedron,* fig. 81. The lines joining the centres of the square faces are axes.

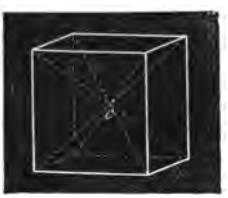

Fig. 81.

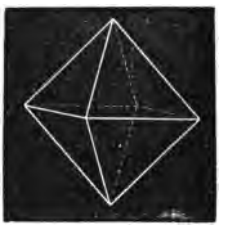

Fig. 82.

It also includes the *regular octahedron,* fig. 82, the axes of which are lines joining the opposite angles. Also the *regular rhombic dodecahedron,* fig. 83, the *regular tetrahedron,* whose faces are four equilateral triangles, fig. 84, and various other forms derived from these by modification or combination.

2°. THE SQUARE PRISMATIC SYSTEM takes its name from the square right prism, the height of which is greater or less than the edge of its base. In this system there are three axes, each of which is at right angles to the plane of the other two. Two are equal, but the third is greater or less than these.

This system includes, besides the *rectangular square prism*, the *octahedron* with a square base, fig. 85, the axes being the two diagonals of the base and the line *cc*.

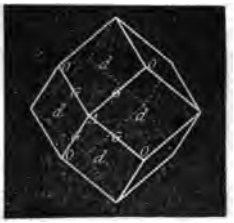

Fig. 83.

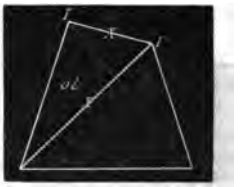

Fig. 84.

3°. The Rhombohedral System has four axes, of which three are equal, in a common plane, and intersect at angles of 60°, the fourth being at right angles to this plane.

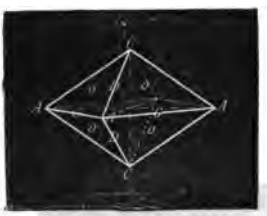

Fig. 85.

Fig. 86.

This system takes its name from the *rhombohedron*, fig. 86, which is one of its principal forms. The principal axis *cc'* joins two opposite angles, while the other three or secondary axes join the middle points of the opposite edges.

This system also includes the *regular dodecahedron*, fig. 87, the faces of which are 12 equal isosceles triangles standing on a common hexagonal base, the three diagonals of which are the secondary axes. It also includes the *right hexagonal prism*, fig. 88, and the *dodecahedron*, with scalene triangular faces, fig. 89.

4°. The Right Prismatic System has three unequal axes, each of which is at right angles to the plane of the other two.

This system takes its name from the *right prism* with a rectangular

base, which is one of its forms. The principal axis is the axis of the prism, and the lines joining the centres of the opposite lateral faces the secondary axes.

Fig. 87.

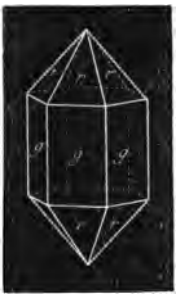

Fig. 88.

Fig. 89.

Another form of this system is the *right octahedron* with a rhombic base, fig. 90, consisting of two right triangular pyramids having a common

Fig. 90.

Fig. 91.

rhombic base. The axis of the pyramids is the principal, and the diagonals of the base the secondary axes.

5°. The Oblique Prismatic System has three unequal axes, two of which are oblique to each other, the third being perpendicular to their plane.

This system takes its name from the *oblique rectangular prism*, whose base is a rectangle with unequal sides, its axis being inclined to the base.

The axis of the prism is the principal, and the lines joining the centres of its opposite lateral faces the secondary axes.

The octahedron, fig. 91, consisting of two scalene triangular pyramids with a rectangle as a common base, belongs to this system.

6°. THE DOUBLY OBLIQUE PRISMATIC SYSTEM has three unequal axes, each of which is inclined to the plane of the other two.

This system includes the *oblique prism* with an oblique parallelogram as a base; the octahedron consisting of two scalene triangular pyramids with an oblique parallelogram as their common base.

The following are examples of the crystalline forms of the several systems:—

1. *Regular system.* Most of the metals, diamond, salt, alum, garnet, fluor-spar, galena.
2. *Square prismatic.* Zircon, tinstone, apophyllite, ferrocyanide of potassium.
3. *Rhombohedral.* Ice, calcareous spar, nitrate of soda, rock crystal, arsenic, antimony, graphite.
4. *Right prismatic.* Sulphur (at low temperature), nitre, iodine, sulphates of potash and baryta.
5. *Oblique prismatic.* Sulphur (by fusion), realgar, sulphate, carbonate, and phosphate of soda, borax, green vitriol.
6. *Doubly oblique prismatic.* Sulphate of copper, nitrate of bismuth.

When the same body is capable of crystallising in different systems, under different conditions, it is said to be *dimorphous.* Sulphur is an example of this.

When two different bodies crystallise according to the same system they are said to be *isomorphous.*

THE METRIC SYSTEM.*

1. THE base of this system is the length, at the temperature of melting ice, of a platinum standard, made in 1798, to represent the ten-millionth part of the quadrant of the Meridian of Paris, as then determined. This length—the '*mètre*' (from *μέτρον*, a measure)—is greater than our yard, being equal to 3 feet $3\frac{1}{8}$ inches; or more exactly, 39·3708 inches. The system is a *decimal* one; *i.e.*, in each table every denomination is ten times greater than that next below it.

2. In the various tables the names of the denominations which are multiples of the unit-measure are formed by prefixing *deca-*, *hecto-*, *kilo-*, and *myria-*, respectively to its name. These prefixes are derived from the Greek words meaning *ten*, *hundred*, *thousand*, *ten-thousand*, respectively.

3. Similarly the names of the denominations which are sub-multiples of the unit-measure are formed by the prefixes *deci-*, *centi-*, *milli-*, derived from the Latin words meaning *tenth*, *hundredth*, *thousandth*, respectively. Hence the following table of—

4. MEASURES OF LENGTH.

	mètres.	inches.	
1 myriamètre	= 10000	= 393708.	
1 kilomètre	= 1000	= 39370·8	= 1093·63 yards, or 5 fur-
1 hectomètre	= 100	= 3937·08	[longs, nearly.
1 decamètre	= 10	= 393·708	= 2 poles, or half-a-chain,
1 mètre	=	39·3708	[nearly.
1 decimètre	= $\frac{1}{10}$	= 3·93708	= 4 inches, nearly.
1 centimètre	= $\frac{1}{100}$	= 0·393708	= $\frac{4}{10}$ or $\frac{2}{5}$ inch, nearly.
1 millimètre	= $\frac{1}{1000}$	= 0·0393708	= $\frac{4}{100}$ or $\frac{1}{25}$ inch, nearly.

N.B.—32 *mètres* = 35 *yards*, to less than one-fifth of an inch.

* By J. J. Walker, M.A., Mathematical Master, University College School.

5. To form an approximate idea of the length of the sub-multiples of the mètre, take a common foot-rule, divided into eighths of an inch. The decimètre is very nearly equal to four inches. The centimètre is a very little longer than three-eighths of an inch; and if the eighth be conceived to be divided into three equal parts, each of these will not sensibly exceed the length of the millimètre.

1 inch = 2·539954 centimètres.
1 yard = 0·91438348 mètre.
1 mile = 1609·3149 mètres.

6. The approximate values in English measures indicated in the table (4) give some useful practical rules for converting lengths expressed in mètres, &c., into their English equivalents, when extreme accuracy is not required.

(*a.*) To convert *kilomètres* into *miles: Multiply by* 5, *and divide by* 8; or, for greater accuracy, *multiply by* 875, *and divide by* 1408 (= 8 × 16 × 11). Thus, 752 k. = 752 × 5 ÷ 8, or 470 miles by the first, and 752 × 875 ÷ 1408, or 467 miles, by the second rule. The latter result is exact to within $\frac{1}{10}$th of a mile.

(*b.*) To convert *mètres* into *yards: Multiply by* 35, *and divide by* 32. Thus, 17 mètres = 17 × 35 ÷ 32 yards = 18 yards $21\frac{3}{8}$ inches.

(*c.*) To convert *decimètres* into *feet: Divide by* 3; or, more exactly, *multiply by* 21 *and divide by* 64. Thus, 7·5 d. = $2\frac{1}{2}$ feet, nearly.

(*d.*) To convert *centimètres* into *inches: Multiply by* 4 *and reject the last figure;* or, more exactly, *multiply by* 63 *and divide by* 160. Thus, 76 c. = 76 × 4 ÷ 10, or 30 inches, nearly; = 76 × 63 ÷ 160, or 29·92 inches, very nearly.

(*e.*) To convert *millimètres* into *inches*, or decimals of the inch: *Multiply by* 4 *and point off the last two figures;* or *multiply by* 63 *and divide by* 1600.

(*f.*) To convert *miles, yards, feet, inches* into Metric equivalents: *Multiply by the divisors and divide by the multipliers*, as given above.

7. SQUARE MEASURE.—The unit of area is that of the square described on a line equal in length to 1 *decamètre*. This is named the "*are*" (from the Latin "*area*," a flat open space). A table of multiples and sub-multiples of this unit is formed on the same principles of nomenclature as the table of measures of length; but in practice these are rarely used, with the exception of the *hectare* = 100 *ares* = 10000 square mètres = $2\frac{1}{2}$ acres, nearly; which is used in measuring large areas, such as fields or farms. For smaller areas, such as building plots, carpenters' work, &c., the square mètre, decimètre, &c., are universally employed.

1 square inch = 6·4513669 square centimètres.

8. For approximate conversion of areal measures, therefore, we have the following rules:—

(*g.*) To convert *hectares* into *acres: Annex a cipher and divide by* 4. Thus, 34 *hectares* = 85 *acres.*

N.B.—10 *ares* = 1 *rood*, nearly.

(*h.*) To convert *square mètres, decimètres*, &c. into *square yards* or *inches: Multiply and divide twice* successively by the figures given in rules (*b*), (*c*), (*d*). Thus, 73 *square mètres* = $73 \times 35 \times 35 \div 32 \div 32$, or $87\frac{1}{3}$ *square yards*, nearly. Again, 13 *square centimètres* = $13 \times 16 \div 100$, or 2 *square inches*, nearly.

(*i.*) *Square decimètres* may be reduced to *square feet* approximately *by dividing by* 9. Thus, 27 *square decimètres* would = 3 *square feet.* More exactly, 1 *square decimètre* = $15\frac{1}{2}$ *square inches.*

(*j.*) To convert *square inches, feet, yards*, and *acres* into their Metric equivalents, the operations in the above rules are to be reversed.

9. MEASURES OF CAPACITY AND CUBIC MEASURE.—The unit of this table is the volume of the cube, each edge or side of which is equal in length to 1 *decimètre.* This measure is called the "*litre.*" * Its equivalent in English measure is 61·027 cubic inches; or (taking 1 gallon = 277·274 cubic inches) 1·76 pints —say 1¾ pints. Besides the *litre*, the only other measure of capacity much used is the *hectolitre* = 100 *litres* = 22·01 gallons. For measuring earth-work, timber, &c., the cubic *mètre* ("*stère*") is employed. The *stère* (στερεός, solid) = 35⅓ *cubic feet*, nearly.

A millilitre or one cubic centimètre is the usual standard of volume in actual chemical work.

1 cubic inch = 16·3861759 cubic centimètres.
1 gallon = 4543·457969 „ „

10. MEASURES OF WEIGHT. — The unit of weight is the "*gramme;*" † but the value of this unit is more easily recollected from the statement that the *kilogramme* (= 1000 *grammes*) is the weight of one *cubic decimètre* or *litre* of distilled water, at its greatest density, and weighed in a vacuum.

1 kilogramme = 15432·349 grains or 2·205 lbs.
1 gramme = 15·432349 „
1 grain = 0·06479895 gramme.
1 troy oz. of 480 grains = 31·103496 grammes.
1 lb. avd. of 7000 grains = 453·59265 grammes.

The average height of the barometer at Paris is 76 centimètres. Reduce this to inches correctly to three places of decimals.—*Ans.* 29·922 inches.

Supposing the quadrant of the meridian of Paris to be 6213 mi. 6 fur. 23 po. 4 yds. in length, calculate the length of the mètre in inches to five places.—*Ans.* 39·37079 inches.

The French Post Office allows 7·5 grammes for a single postage; the

* From the mediæval Latin "*litra*" (λίτρα), a liquid measure.
† From γράμμα, used in later Greek in the sense of a small weight.

English ½ of an oz. Avoir. By how many grains does the French exceed the English allowance?—*Ans.* 6⅝ grains.

How many hectolitres = 1 cubic mètre? A tank is 37½ decimètres long by 25 wide, and 18 deep. How many gallons would it hold?—*Ans.* 3714 gallons.

The length of the tunnel through Mont Cenis will be about 12.22 kilomètres. What will this be in miles, very nearly?—*Ans.* 7·6 miles.

The diameter of bore and weight of a piece of French ordnance are given as 27 centimètres and 22,000 kilogrammes. Give the corresponding measure and weight in inches and cwt.

The pressure of the atmosphere at the average height of the barometer is 14¾ lbs. Avoir. to the square inch. What would be the corresponding pressure in kilogrammes to the square centimètre?—*Ans.* 1·04 k.

GENERAL OPERATIONS.

In all experiments it must be carefully borne in mind that each *operation* is to be performed exactly as described, that the utmost attainable accuracy and *precision* is to be striven for, and that such expressions as "near enough" are to be banished from the beginner's vocabulary.

As all experiments require the performance of certain operations, which are known by technical names, it is well before commencing the study of particular bodies, to familiarise oneself with the meaning of these names, and the manner of conducting the processes designated by them.

Pulverisation, or *powdering*, is performed in a mortar, and is done chiefly to give greater surface to a body, so that other substances may act on it more quickly. (*Ex.*) Powder some brown "rock salt," or some "potassic dichromate."

Solution.—(*Ex.*) Stir some of the powdered rock salt with water in a glass, the greater part will dissolve, *i. e.*, mingle so intimately with the liquid that it no longer remains visible, having lost its solid form. Observe that the brown matter contained in the rock salt remains *undissolved*, put the glass containing the salt and water on one side, and (*Ex.*) put into a test tube some powdered marble, and boil it with water, it will not dissolve; add either hydrochloric acid, nitric acid, or acetic acid, it dissolves with *effervescence*. Observe, that though a body may be insoluble in one menstruum, it may dissolve in another.

Decantation.—(*Ex.*) Take the glass in which the rock salt and water were mixed, and carefully pour off (*i.e.* decant) the clear liquid from the sediment. This operation is best performed by first slightly greasing the top of the glass, and then pouring the liquid down a glass rod, as shown in the cut (Fig. 92).

Filtration.—When it is desired to separate a liquid from a solid in a very perfect manner, *filtration* is adopted. A round piece of unsized paper * is folded twice at right angles, and then one of the folds so opened

* For most filtrations the common white filtering paper of the shops is good enough; but if the solid which is to be removed from a liquid is in a very fine state of division (*e.g.*, oxalate of lime), it will run through the comparatively large pores of this paper. In such cases use "Swedish paper."

out as to make the paper assume the form of a hollow cone. This paper is then put in a funnel (Fig. 92) and wetted with distilled water, and the liquid which is to be filtered poured carefully on to one side of the paper by the help of the glass rod. The filter should never be more than three quarters filled. (*Ex.*) Pour on a filter so prepared the last portions of the liquid containing the sediment from the rock salt; the clear solution of salt will run through, while the insoluble earthy bodies will remain on the paper. Taste the *filtrate* (the portion run through) to assure yourself that the *salt* has not been removed by filtration.

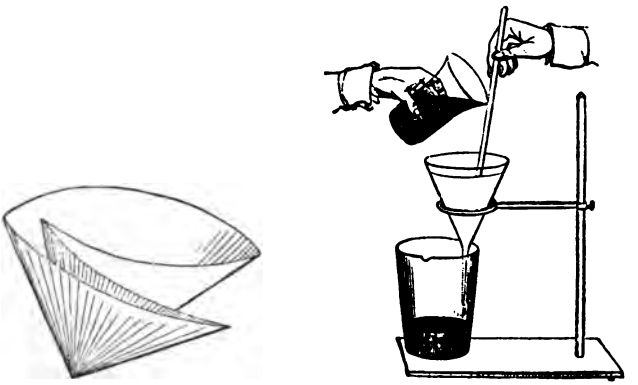

Fig. 92.

Evaporation (sending away as vapour).—Put the *clear* solution of salt into an evaporating basin (Fig. 93), and apply heat so as to drive water away in the form of steam, the liquid will become smaller in bulk, and as

Fig. 93.

no salt goes away with the steam the solution will get more concentrated; ultimately the whole of the water will be expelled and a dry mass of white salt left.

Distillation is resorted to where it is desired to purify a liquid from solid bodies which it holds in solution, or from other liquids with which it may be mixed. (*Ex.*) Put a solution of potassic dichromate into a

retort (Fig. 94), insert the neck of the retort into a flask which is kept cold by water in the basin, over the neck of the retort place an oblong-shaped piece of filtering paper which is to be kept wet by water dripping on its upper edge from the funnel, the neck of which is nearly closed by a plug of filtering paper. The excess of water will drip from the lowermost corner of the paper, and can be caught in a glass. When these things are properly arranged, apply a gentle heat to the liquid in the retort which will soon begin to boil, pure water vapour being given off. This vapour coming into the neck of the retort gives up a great deal of its heat to the water which is running over the paper on the outside, and is thereby *condensed* into water, which trickles down into the flask placed to receive it. If the distillation has not been too rapid the *distillate* will be perfectly colourless, but if spirting has taken place from too violent an *ebullition*, it will have a marked yellow tint: in the latter case it must be redistilled.

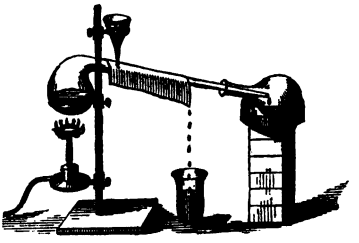

Fig. 94.

Sublimation is the distillation of solid bodies. (*Ex.*) Heat a fragment of dry ammonic chloride in a test tube, continuing the application of heat until the whole of the salt has volatilised and again condensed in the upper and colder parts of the tube. Comparatively few solids are sufficiently volatile to admit of being sublimed.

Precipitation. — When any substance causes the separation of solid matter from the solution of another body, that solid matter being thrown out of solution is called a *precipitate;* the thing causing the precipitation is named the *precipitant.* (*Ex.*) Add a solution of carbonate of soda to one of chloride of calcium in a test tube, a white precipitate of carbonate of lime will be formed; boil the liquid, the precipitate will shrink together and settle readily.

Note. In all cases of precipitation, if the quantity of precipitate be very small it may remain suspended in the liquid for a considerable time, but will in such a case render the fluid opalescent; and this destruction of transparency proves the formation of solid matter as well as the collection of a deposit at the bottom of the vessel would.

Washing.—After a body has been precipitated, it needs washing if required in a pure form; this operation of washing is one of great importance, and must be performed thoroughly when directed to be done at all. Washing of a precipitate is effected either by decantation or filtration.

To do it in the first way: stir up the precipitate with a large quantity of distilled water in a tall narrow vessel, then allow it to settle, and decant the supernatant fluid; repeat this until some of the wash water will neither leave any residue on evaporation, nor give any precipitate with a reagent, which would give one with the impurities originally present.

Washing by filtration is generally the preferable method. (*Ex.*) Throw the precipitate of carbonate of lime on a filter which has been first wetted with water, allow *all* the liquid which will do so to run through; then stir it up with a jet of distilled water from the squirt bottle, and at the same time take care that the upper part of the filter is washed by the stream. Allow this portion to run through completely, and repeat the operation of washing till a portion of the clear wash water will give no precipitate or cloudiness with a solution of nitrate of silver, proving that all the soluble chlorides have been removed.

Ignition is the rendering of a body fiery hot; it is performed in porcelain or platinum crucibles, if the quantity of material operated on is small, and a lamp is to be used as the source of heat; or in earthen crucibles if the quantity is large and a fire is to be employed. (*Ex.*) Put into a porcelain crucible some chips of wood, put the cover on, and support the whole over a bunsen gas lamp (or ordinary spirit lamp) by means of the wire triangle (Fig. 95). Continue the application of heat till flame

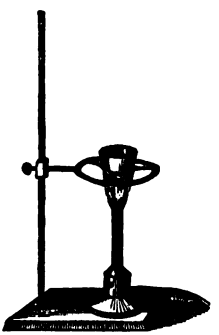

Fig. 95.

Fig. 96.

ceases to issue from the crucible; allow the whole to cool, and observe that the wood has been converted into charcoal by ignition. Sometimes very small quantities have to be intensely ignited: in this case the material is supported on a loop of platinum wire in the flame of the blow-pipe.

In applying heat to glass or porcelain vessels, do so cautiously at first, keeping the lamp or the vessel moving as is most convenient, to ensure the

whole bottom of the flask, &c., being evenly heated. The flame should never play directly on the bottom of any glass vessel larger than a test tube: flasks and beakers should stand on sand or on wire gauze. In all cases be sure to have the outsides of the vessels to be heated quite dry, and avoid spirting water on them while hot, or they will certainly crack. Avoid allowing glass vessels to become dry inside while being heated.

COLLECTING AND TRANSFERRING GASES.—The method of collecting a gas at the water pneumatic trough is obvious from the cut, fig. 96. When one vessel is filled with a gas, slip a small cheeseplate or gas tray under its mouth while still in the water and lift the two out together: the least depth of water will effectually preserve the gas for a short time (½ to 24 hours). Wide mouth bottles can be closed by their greased stoppers, and stood aside mouth downwards. Vessels with ground edges can be closed by a wet glass plate. Note: In all cases avoid lifting a vessel of gas from the water before closing its mouth.

The decantation of a gas from one vessel into another is effected by depressing the one containing the gas well below the surface of the water in the trough and below the mouth of the second vessel, which is full of water, and then cautiously pouring the gas up through the water. Practise this with air.

When the mercury trough is used the manipulations are the same as when water is employed, but as mercury is opaque and very heavy there is more difficulty. The best kind of trough for most purposes is one of about a foot long, 6 inches wide, and 5 inches deep (outside), hollowed out of a block of solid beech, and well varnished; it should have a groove 1¼ inch wide and 2 inches deep along the middle, and a wide well 3 inches deep, with a flat bottom covered with thick sheet caoutchouc at one end. The trough should be stood in a large wooden tray to catch any spillings. The operator should lay aside his gold or silver chain, watch, &c., or they will be spoilt by the inevitable splashes. Indeed, he had better always wear an apron and sleeves.

If it is wished to collect a gas by displacement of air, it must be evolved rather rapidly, and led to the top, or bottom, as the case may be, of the receiving vessel, the mouth of which is loosely covered by a card to prevent draughts, and from blowing the gas out as fast as it collects.

IGNITING LONG TUBES.—For this purpose you may make use of the gas furnace shown on p. 21, or the sheet-iron trough furnace shown on p. 17. In the latter case you should have an abundant supply of charcoal ready burning in a grate, and then fill the trough with the hot fuel by the help of tongs. Beware of the sparks which fly off in great numbers from charcoal which is at all damp. The gas furnace is by far the best: the mode of using it will be obvious on inspection. If the tube to be ignited be of

glass, it should be supported in a little gutter made of sheet iron, the bottom of which is covered with asbestos or whiting.

Explosion of gases in the eudiometer is effected by passing an electric spark between the two wires at the top of the tube. The source of the spark may be either a charged Leyden jar, or a small Ruhmkorf's coil, as shown in the cut, on page 135. In either case the outside of the eudiometer must be dry, or the discharge will take place through the film of moisture. Take care not to have the tube more than one quarter full of a mixture which explodes with any great degree of force; and if you hold it in your hand while exploding the gases, have three or four folds of a strong cloth between your skin and the glass.

PREPARATION OF APPARATUS.

BORING AND FITTING CORKS.—The corks must be sound, and, if of large size, *must* have their grain at right angles to their length. Choose a cork which seems just too large for the neck of the bottle, &c., roll it under the foot to make it soft, wash it; see that it will squeeze into the neck of the bottle, and that it obviously touches all round; dry it, and then bore the necessary holes into it by means of the cork borers, or by a ratstail file with a sharp point. If it is to be used in an apparatus for chlorine, or other corrosive gas, soak it in melted paraffin to close all pores, and to enable it to withstand the action of the gas. The "gas candles" are a convenient form in which to buy paraffin.

India-rubber corks (!) are in every respect better than bark ones, but are expensive; they should be used for the construction of such apparatus as is constantly in use; they can be bored by the ordinary cork-borers moistened by spirit.

BENDING AND CUTTING GLASS TUBE.—Small glass tube can be readily bent after first softening it in the flame of a gas or spirit lamp. The best gas flame is a fish-tail burner. Hold the tube in the smoky part of the flame, so as to heat a considerable length at one time; turn the tube round constantly, and when it has become *quite* soft, bend it to the required angle at one motion. Large glass tube can only be bent and drawn out before the flame of a blowpipe of considerable size, and supplied with air by bellows. Glass tube is cut by scratching it with a triangle file, and then *pulling* the parts asunder. These two simple processes of boring and fitting corks, and cutting and bending small glass tube, will enable the student to fit up most of the apparatus he requires.

In fitting up the apparatus for examining gases, take the trouble to make the connecting glass tubes all come to the same height above the table. The various pieces can then be joined by short bits of india-rubber tube without the use of blocks. In the wood-cuts in the body of the work all apparatus is so drawn. The following pieces of apparatus should be put together with care, and always kept clean and ready for use.

Figs. 97 and 98.—Apparatus for preparation of gases in the cold; two sizes, the larger bottle about 1½ pint capacity.

Fig. 97.

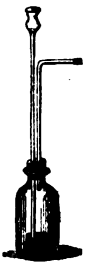

Fig. 98.

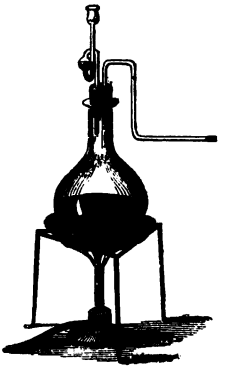

Fig. 99.

Figs. 99 and 100.—For preparation of gases when the aid of heat is required. The flasks *must* be thin and well annealed. German flasks are the best. The larger flask is supposed to be of 30 oz. capacity, the smaller of 10 oz.

Fig. 101.—Washing and drying bottles. Gases are passed through these to remove spray or moisture. In the first case they contain pumice stone (omitted in the drawings for the sake of showing the tubes,) moistened

Fig. 100.

Fig. 101.

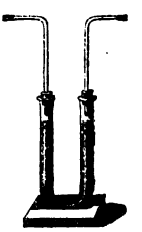

Fig. 102.

with water; and in the second case, pumice soaked in oil of vitriol, which absorbs vapour of water.

Fig. 102.—U tubes for drying gases completely. They are filled with pumice soaked in oil of vitriol, when the gas to be dried is not acted on by that body, or with strongly dried calcic chloride in *small* fragments, or in special cases (*e.g.*, ammonia) with potash.

They are fixed in square blocks of wood by cementing their bends into a groove by "soft cement." It will be found useful to keep one for chlorine, another for hydrogen, &c.

Fig. 103.—The preparation of small quantities of gases, especially of those which, like oxygen, require a very high temperature. The gene-

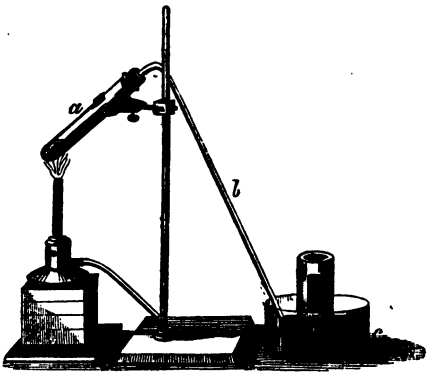

Fig. 103.

rating tube should be of very infusible glass. A small round-bottomed flask may often be substituted for the test tube with advantage.

Fig. 104.—Bottle gas-holder. A large wide-mouth glass bottle, (not necessarily or even generally so large as that represented,) such as a wide-mouth "Winchester quart," is fitted up in the way shown. (*a*) is a funnel of tin plate fastened to a tube of the same material, or simply stepped into a wide stout glass tube, and fixed thereto by a collar of india-rubber tube. (*c*) is an exit tube having a three-inch length of india-rubber tube; which can be compressed by a pinch cock (*b*), as shown, or better, by a small screw clamp (price 1*s*.) (*d*) is a syphon tube similarly provided, and which must on no account be longer than the one shown in the figure. To use this apparatus for the collection of a gas, fill the bottle with water, and connect (*c*) with the apparatus from which the gas is being evolved, taking care that both clamps (*bb*) are opened. As the gas enters (*c*), water will run out through (*d*), the mouth of which should be kept at the level of the water in the bottle by raising or lowering it as occasion requires. When sufficient gas is collected, close both clamps, and pour water into (*a*). The included gas will now be compressed by a force proportional to the height of the water in (*a*) over that in the bottle

(1 lb. per square inch for each 27 inches difference); therefore when the clamp on (*c*) is opened it will rush out, at a speed which can be regulated with great nicety by compressing the flexible tube more or less by the screw.

Metal gas-holders of a very convenient form (Pepys') are sold by chemical dealers, but the price is high.

These separate pieces of apparatus are connected by slipping the two ends of a bit of caoutchouc tube over the opposing ends of the glass tubes. If the caoutchouc tube fits tightly it makes an excellent joint, which can be rendered still better by twisting a bit of copper wire round that part which is over the glass.

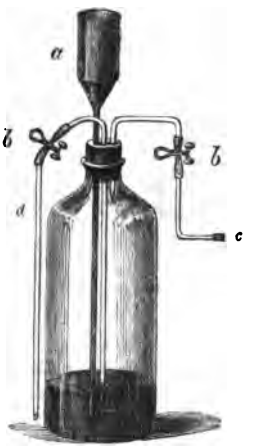

Fig. 104.

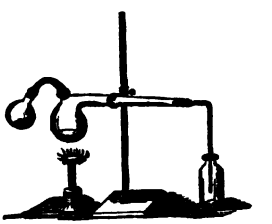

Fig. 105.

Where two glass tubes of unequal size have to be connected, as when a delivery tube has to be fixed to the beak of a retort, a bit of fleshy india-rubber tube is slipped on to the smaller one, and then squeezed into the larger one,—is used like a cork, in fact, fig. 105.

Coating retorts, tubes, &c., to render them capable of withstanding a very high temperature :—mix the ready-ground Stourbridge clay, which is sold by the dealers, into a stiffish paste with water; wet the flask, &c., outside, smear it over with a bit of the moist clay, and then plaster the clay evenly on, to the thickness of about $\frac{1}{2}$ of an inch. Set aside in a slightly warm place for at least twenty-four hours, and then, if the clay *looks* quite dry, you may complete the drying on a sand bath or in an oven.

APPARATUS AND CHEMICALS.

THE FOLLOWING LIST OF APPARATUS IS COMPILED FROM THE ILLUSTRATED AND PRICED CATALOGUES OF—

Messrs. JAMES HOW, 2, Foster Lane, London;
,, J. J. GRIFFIN, Garrick Street, Covent Garden;
,, JACKSON & TOWNSON, 89, Bishopsgate Within,

who all sell equally good apparatus at about the same prices. Griffin's complete catalogue will be found very useful by persons living in the country who are unable to select personally the articles they require.

Caoutchouc corks are best obtained from Mr. Sheath, of 89, City Road, E.C., as those supplied by the chemical dealers are too hard.

NECESSARY ARTICLES.	s.	d.
1 retort stand 3 rings .	6	0
Screw clamp for same, like that shown in fig. 103 .		
2 tripod stands (figs. 99 and 100) 0/10 and 1/0 . .	1	10
1 test tube rack . .	1	4
* 2 Bunsen's gas burners, 1 small size at 2/9, 1 large one 6/0 (both with rose burners) . . .	8	9
1 set of 8 beakers, 4 to 40 oz.	5	0
1 doz. narrow-mouth stoppered bottles, German glass 4 oz.	4	6
1 doz. ,, . 8 oz.	6	0
1 doz. ,, . 12 oz.	8	0
1 doz. wide mouth do. do. 2 oz.	4	6
1 doz. do. . . 4 oz.	5	6
½ doz. wide mouth English stoppered bottles for gas receivers, 3 of 1 pint and 3 of 1 quart capacity .	8	3

FLASKS, GERMAN—	s.	d.
2 of 3 oz. capacity . .	0	8
2 of 6 oz. ,, . . .	1	0
2 of 10 oz. ,, . . .	1	4
2 of 16 oz. ,, . . .	1	6
2 of 25 oz. ,, . . .	1	10
2 of 30 oz. ,, . . .	2	0
FUNNELS—		
1 each of 1½, 2, 2½, 3, and 4 inches diameter . .	1	4
Thistle funnels with long tube (for hydrogen apparatus, &c.), 6 at 0/6 .	3	0
Safety funnels with bulb (for chlorine apparatus), 2 at 0/9	1	6
Gas jars with stoppered necks for burning iron in oxygen, &c., 2 at 4/0 . . .	8	0
GLASS TUBE—		
2 lbs. assorted sizes of soft French	3	0
2 lbs. German combustion tube, including a stick or two of quill size . .	4	0
½ lb. glass rod for stirrer, &c.	0	9
Pipette with bulb . .	0	6

* Where gas is not procurable, spirit lamps must be substituted.

One single wick glass lamp 3 oz. cap. . . 1/0.
And a metal argand lamp . . . . 10/0.

The spirit to be used with these is methylated spirit at 5/6 a gallon; or, where this is not to be bought, methylated finish, which can be got at any varnish maker's at about the same price.

	s.	d.
Washing bottle with jet and blowing pipe . . .	1	6
RETORTS—		
3 plain . 2 oz. capacity	0	9
2 ,, . 10 oz. ,,	1	4
1 tubulated 4 oz. ,,	1	10
1 ,, 12 oz. ,,	1	4
TEST TUBES —		
3 nests of 6 each . .	2	0
Cylindrical test glasses, 3 of 2 oz. and 3 of 6 oz. capacity	2	9
Gas tube graduated in 50 cu. cent.	2	6
CRUCIBLES—BERLIN PORCELAIN—		
1 each of Nos. 0, 1, and 2 .	2	0
Round London earthenware, 3 each of four smallest sizes, with covers about	1	6
EVAPORATING BASINS—BERLIN PORCELAIN—		
1 each of 2 oz., 3 oz., 6 oz., 16 oz., and 40 oz. . .	6	2
Mortar and pestle Wedgwood ware, 6 inches diameter	3	9
Thermometer, marked on stem from —10° to 300° C.	6	0
Sheet iron furnace for heating long tubes (Liebig's combustion furnace) .	4	0
Crucible tongs, small . .	1	0
,, ,, (forging tongs) 18 in.	3	0
Blow pipe, Black's . .	1	0
U tubes, 3 with 9 in. limbs	3	0
,, 3 ,, 6 in. ,,	2	3
Filtering paper cut in circles, 1 packet of $3\frac{3}{4}$ in. diam. and 1 of $5\frac{1}{4}$ in. . .	1	4
Set of 6 cork borers . .	3	6
2 test tube brushes . .	0	6
3 tin deflagrating spoons .	1	0
1 triangle and 1 ratstail file	1	0
6 doz. good corks, assorted sizes	4	0
6 smooth-necked wide mouth bottles for making gas apparatus, washing bottle, &c. :—of 6 oz. capacity .	1	0
4 of 12 oz. capacity . .	1	0
2 of 30 oz. ,, . .	0	8
Round stone ware pneumatic trough with bee-hive shelf (or a small earthen footpan will serve excellently).	6	10
Small screw clamp for compressing india-rubber tube	1	0
2 feet each of the various sizes of india-rubber tube, from $\frac{1}{8}$ to 1 in. diameter, about	6	0
1 doz. assorted ground glass plates	1	0

THINGS USEFUL, BUT NOT ESSENTIAL.

	s.	d.
Iron mortar, 6 in. diameter	4	6
Small retort stand with a spring clip (1/6) tube holder	4	6
Wooden clamp for supporting retorts, &c. . . .	3	6
$\frac{1}{2}$ litre glass measure .	5	0
Glass-blower's table and lamp to be used with oil or gas . . .	4	4	0
Black's portable furnace for heating crucibles, &c.	4	4	0
Pepys' gas-holder, 4 gall.	1	1	0
Hoffman's gas combustion furnace (shown p. 21)	5	5	0
Set of 9 flat glass basins	0	3	6
Liebig's condenser for condensing volatile liquids when distilled .	0	10	6
Balance, as good as you can afford. Oertling, of Moorgate Street, makes a reliable instrument for about £3 3s., a set of good weights (and bad ones are useless) will cost another 35s., in all nearly	5	0	0

		£	s.	d.
Small Ruhmkorf's coil, such as is used for exhibiting vacuum tubes; it should give a quarter inch-spark. A bichromate battery to work it; the two, about		3	0	0

CHEMICALS, &c.

The quantities given in the following list are intended as a guide to persons living in places where fresh supplies are not readily obtained; in other cases it is, of course, not necessary to keep a stock on hand. The names used are those by which the preparations are known in commerce:—

	QUANTITY. lb.	oz.	PRICE. s.	d.
Acid, acetic	0	8	0	6
,, arsenious	0	2	0	3
,, hydrochloric, pure	8	0	6	0
,, hydrochloric, commercial	16	0	4	0
,, hydrofluoric, in gutta-percha bottle	0	2	1	3
,, molybdic	0	½	1	0
,, nitric, pure	5	0	5	0
,, oxalic, com.	0	4	0	6
,, phosphoric anhydrous	0	1	2	6
,, pyrogallic	0	½	2	0
,, sulphuric, pure	1	0	1	0
,, ,, com.	20	0	5	0
,, ,, Nordhausen	1	0	2	0
Alcohol, methylated, ½ gallon			3	0
Ammonia	4	0	3	0
* ,, carbonate	0	4	0	6
* ,, chloride sal-ammoniac	2	0	1	6
,, nitrate	1	0	2	0
* ,, phosphate	0	1	0	6
Antimony, metallic	0	4	0	3
,, sulphide (native)	1	0	1	0
Arsenic, metallic	0	1	0	4
Asbestos	0	2	1	0
*Barium, chloride	0	4	0	8
,, oxide (baryta)	0	2	1	6
Bismuth, metallic	0	1		
Borax	0	2	0	4
Bromine	0	1	2	0
Calcium, chloride, com.	3	0	1	6
,, fluoride / fluorspar	0	8	0	2
Charcoal, animal	0	8	0	3
Copper turnings	0	4	1	0
,, oxide	0	2	1	0
Indigo sulphate	0	2	0	4
Iodine	0	2	2	6
Iron filings	1	8	0	6
* ,, sulphate (proto)	0	4	0	2
,, sulphide	1	0	0	8
*Lead, acetate	0	2	0	3
,, oxide (litharge)	0	8	0	3
Litmus	0	1	0	3
Litmus paper, about 6d. worth, red and blue			1	0
Magnesium sulphate	0	4	0	4
* ,, wire			1	0
Manganese black oxide	3	0	0	9
Mercury	10	0	25	0
* ,, bichloride	0	1	0	6
,, cyanide	0	1	1	0
,, red oxide	0	2	1	6
,, subnitrate (sol.)	0	2	0	6
Platinum wire for blow pipe			1	0
* ,, bichloride (tetrachloride)	0	⅛	3	0
*Potash, caustic	0	8	1	9

CHEMICALS, &c.—*continued.*

	QUANTITY.		PRICE.	
	lb.	*oz.*	*s.*	*d.*
Potassium, bichromate	0	1	0	3
,, metallic	0	½	1	6
,, carbonate pure	0	4	2	0
,, chlorate	1	0	2	0
,, cyanide (com.)	0	2	0	6
,, iodide	0	2	2	0
,, nitrate, (com.) saltpetre	2	0	1	0
* Potassium, silicate soluble glass	0	2	0	4
* Silver, nitrate	0	2	8	0
* Soda, caustic	1	0	2	6
* ,, phosphate	0	2	0	4
Soda Lime	1	0	2	0
Sodium, metallic	0	1	1	0
,, acetate, com.	0	8	0	6
,, carbonate pure anhyd.	0	3	1	0
Sulphur	1	0	0	3
Tin, metallic	0	4	0	6
,, binoxide	0	2	0	8
* ,, protochloride	0	2	0	4
Zinc, metallic granulated	2	0	1	6

The above re-agents can be obtained in a state of great purity, and at a moderate price, from Messrs. HOPKINS & WILLIAMS, New Cavendish Street, W.

Those which are marked with an asterisk are sold in a solid form, and require to be dissolved for most purposes. One ounce of the solid dissolved in eight ounces of distilled water, and filtered into a bottle, will be found a convenient strength. The caustic alkalies must be filtered through a loose plug of asbestos placed in the neck of a funnel.

"Soft cement," which is used for fixing tubes to their supports, &c., can be bought for 1*s.* 6*d.* per lb., or made by melting together 1 oz. of beeswax, 4 oz. of resin, and then stirring in 1 oz. of well dried brick dust or red ochre.

Distilled water can be bought for about 6*d.* a gallon. It is very troublesome to prepare it.

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THE END.

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